ANNUAL REVIEW OF NUCLEAR SCIENCE

VOLUME 1

1952

PUBLISHED BY

ANNUAL REVIEWS, INC.
IN CO-OPERATION WITH THE
NATIONAL RESEARCH COUNCIL
OF THE NATIONAL ACADEMY OF SCIENCES

ON SALE BY

ANNUAL REVIEWS, INC.
STANFORD, CALIFORNIA, U.S.A.

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FOREIGN AGENCIES

H. K. Lewis & Company, Limited
136 Gower Street
London, W.C. 1

Maruzen Company, Limited
6 Tori-Nichome Nihonbashi
Tokyo

PRINTED AND BOUND IN THE UNITED STATES OF AMERICA BY
GEORGE BANTA PUBLISHING COMPANY

PREFACE

Early in 1950, the Committee on Nuclear Science of the National Research Council decided to sponsor the preparation of a series of annual review volumes covering the most important developments in the fields of nuclear science each year. The Committee members agreed that a collection of critical appraisals of each year's progress in the various fields of nuclear research in a single annual volume would be of great value to all of those interested in this rapidly developing field. This volume is the first in the series and covers developments in nuclear science during 1950.

The direct responsibility for assembling the manuscripts for this first review volume was assigned to the Committee's Subcommittee on Publications and Information. In view of the broad scope of the subject matter, the members of the Committee on Nuclear Science agreed to serve as the editorial board for the first volume. Each Committee member has made suggestions as to the topics to be covered and has assisted in editing those sections which fell in his special field of interest.

It is recognized that this first volume does not represent comprehensive coverage of all important developments in nuclear science during 1950. Probably no single volume could. The task of authors of papers in this volume was particularly difficult since they were asked to cover in the limited space assigned to them not only the most outstanding developments during 1950, but also sufficient background material to make possible a critical appraisal of the current status of the subject matter covered. This volume should be regarded as the first in an annual series, the plan for which calls for the various fields of nuclear science to be covered periodically, keeping pace with major developments in all aspects of nuclear research.

When consideration was being given to plans for publishing this volume, advice was sought from Annual Reviews, Inc., which has had extensive experience in issuing annual review series in a number of scientific fields. During the discussions which followed, Annual Reviews expressed willingness to assume responsibility not only for publishing this volume, but for all the work involved in issuing a series of annual review volumes in the nuclear science field. Accordingly, arrangements have now been concluded between the National Research Council and Annual Reviews whereby Annual Reviews will assume the responsibility for the future volumes of this series, beginning with Volume 3. Annual Reviews will also publish Volume 2 in this series, which has been prepared in accordance with plans drawn up by the National Research Council. The Editor commencing with Volume 2 will be James G. Beckerley, with Martin D. Kamen, Donald F. Mastick, and Leonard I. Schiff serving as Associate Editors.

It would be impossible to name individually all of those who have contributed materially to the planning of this volume It is a pleasure to

acknowledge the assistance of the following in selecting topics, suggesting prospective authors, and reviewing the manuscripts: H. A. Bethe (Cornell University), F. G. Brickwedde (National Bureau of Standards), R. H. Burris (University of Wisconsin), D. R. Charles (University of Rochester), R. E. Cleland (National Research Council), M. Deutsch (Massachusetts Institute of Technology), C. L. Dunham (Atomic Energy Commission), S. G. English (Atomic Energy Commission), B. T. Feld (Massachusetts Institute of Technology), H. L. Friedell (Western Reserve University), C. S. Garner (University of California), R. C. Gibbs (National Research Council), M. G. Inghram (University of Chicago), J. W. Irvine (Massachusetts Institute of Technology), L. H. Johnston (University of California), M. O. Lee (National Research Council), U. Liddel (Office of Naval Research), E. M. MacMillan (University of California), J. P. Marble (National Research Council), W. F. Meggers (National Bureau of Standards), W. A. Noyes, Jr. (National Research Council), R. T. Overman (Oak Ridge National Laboratory), P. S. Owen (National Research Council), P. B. Pearson (Atomic Energy Commission), M. Schein (University of Chicago), G. T. Seaborg (University of California), F. Seitz (University of Illinois), and A. K. Solomon (Harvard University).

Special acknowledgment is due to Dr. Dwight E. Gray of the Naval Research Section, Library of Congress, for his indefatigable efforts in assembling the material for this volume and to Dr. Donald F. Mastick of the Atomic Energy Commission's Technical Information Service for his invaluable assistance in handling the myriad details of editing and publication. Finally, it is a pleasure to acknowledge the assistance of Carol F. Kupke of the staff of Annual Reviews, Inc., who has kindly assisted in all matters bearing on the preparation of this volume for the printer.

The contents of this volume have been cleared with respect to security by the appropriate authorities.

ALBERTO F. THOMPSON
Chairman of the
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THEORY OF FISSION PROCESS, *J. A. Wheeler*
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MESON PHYSICS

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The year 1950 saw tremendous advances in the laboratory study of mesons. It was the first year in which the accelerator physicists outdistanced the cosmic ray physicists in so far as their contributions to our understanding of the properties of mesons, the character of their production, and the nature of their interaction with nucleons are concerned. The fact that much greater intensities of artificially produced mesons were available was beginning to make itself felt in a significant and impressive way. It was true, of course, that the laboratory study of mesons was restricted to energies less than about 100 M.e.v. and that higher energy mesons were still the monopoly of cosmic ray research. However, the possibility of performing more controlled, more accurate, and more searching experiments in the laboratory reaped a rich harvest of outstanding accomplishments in 1950. The cyclotron and synchrotron at Berkeley still led the procession, but Rochester and Columbia with their cyclotrons, Cornell and the Massachusetts Institute of Technology with their synchrotrons, and Illinois with its betatron were rapidly catching up.

We propose in this chapter to devote our major attention to the experimental results obtained with accelerator-produced mesons and to refer only occasionally to the cosmic ray material. We shall do so because the former experiments have led to some novel and firm conclusions whereas the latter experiments, while adding appreciably to the amount of existing experimental data, have not particularly clarified the situation over that prevailing a year ago (except for the more definite demonstration of the existence of new types of mesons). Besides, the cosmic ray results will be discussed more fully in the chapter on "Cosmic Rays." We shall not enter into any detailed theoretical considerations, but shall merely indicate the possible theoretical interpretation of an experimental result wherever it exists. Our discussion will be given under the following headings: Photonic Production of π-Mesons; Nucleonic Production of π-Mesons; Properties of π-Mesons; Nuclear Interaction of π-Mesons; Properties of μ-Mesons.

Photonic Production of π-Mesons

We start with the photonic production of π-mesons because it was in this field that some of the important discoveries of 1950 were made. Moreover, the theoretical interpretation of the photonic production experiments is more clearcut than that of the nucleonic experiments, thereby permitting some definite conclusions to be drawn regarding the nature of the π-meson field and the character of the π-meson-nucleon coupling. Since no direct cosmic ray experiments have been performed with photon-produced mesons, our discussion will necessarily be limited to the accelerator experiments.

Production of charged π-mesons in photon-nucleus collisions.—The first observations on the photonic production of charged π-mesons were made in 1949 by McMillan *et al.* (1) using carbon as a target. The Berkeley synchrotron (with an energy of 335 M.e.v.) was the source of γ-rays and the charged π-mesons were detected by means of photographic emulsions. A meson energy spectrum was measured at 90° with respect to the incident photon beam and a broad distribution was found with a maximum at about 40

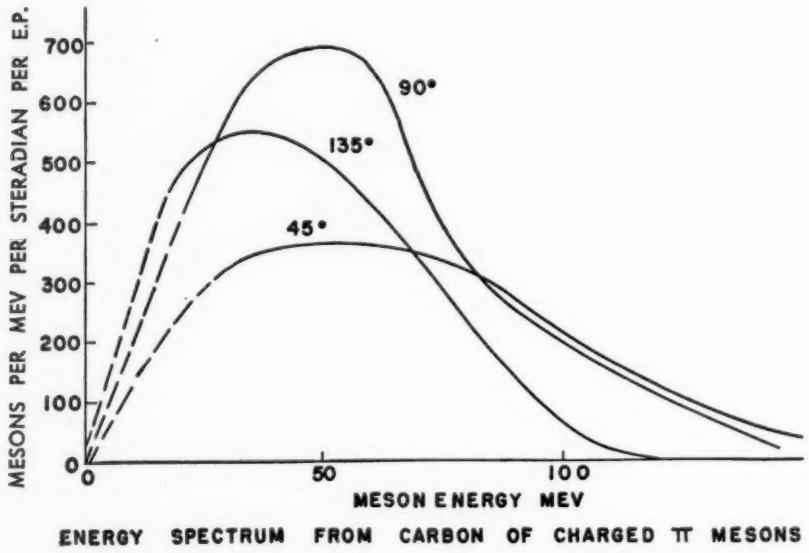

FIG. 1. $\pi^{\pm}$ Energy spectra from γ-rays on carbon at three angles (peak photon energy = 335 M.e.v.).

M.e.v. It was also found that the π^-/π^+ ratio in the energy region 43 to 59 M.e.v. was 1.7 ± 0.2 and that the measured angular distribution was consistent with isotropy in the center of mass system. Assuming isotropic production for mesons of all energy, a meson production cross section of $5 \cdot 10^{-28}$ cm.^{2} per equivalent photon per carbon nucleus was derived (an equivalent photon is defined as the integrated beam energy divided by the maximum energy).

Peterson (2) pursued the photographic method further and obtained meson spectra at angles of 45°, 90°, and 135° from carbon for the same upper limit on the *Bremsstrahlung* γ-rays as the previous work; his results are given in Figure 1. Peterson's absolute cross sections/steradian per nucleus per equivalent photon are given in Table I and may contain a systematic error of 35 per cent. The total cross section is deduced as $3.9 \cdot 10^{-28}$ cm.$^2 \pm 40$ per cent per carbon nucleus per equivalent photon. Table II shows the π^-/π^+ ratio obtained by Peterson at the three angles and also the corresponding

TABLE I

Angle (lab.)	$d\sigma/d\Omega$ (in units of 10^{-29} cm.^{2})
45°	2.42 ± 0.21
90°	3.75 ± 0.17
135°	2.75 ± 0.20

mean meson energies. Peterson's meson spectrum at 90° agrees well with the earlier work, but his π^-/π^+ ratio appears to disagree.

Later cloud chamber work by the Cornell group (3) provides strong evidence for a π^-/π^+ ratio even smaller than Peterson's (although within the experimental error). The Cornell group measures a ratio of 1.1 ± 0.1 for mesons in the energy range 50 to 75 M.e.v. from a carbon target at 135° with respect to the photon direction; on the other hand, the π^-/π^+ ratio is $2.4 \pm .3$ from a beryllium target. The difference between the carbon and beryllium ratios can certainly not be explained by the extra neutron in the beryllium but rather indicates that the relative binding energies of the initial and final nuclei play an important role in the production process. This type of explanation is also favored by the low π^-/π^+ ratio in carbon since the theoretically predicted ratio for free nucleons (for spin 0 π-mesons) exceeds 2 and the motion of the individual nucleons in the carbon nucleus does not appreciably alter this a priori expectation [cf. Brueckner (4)].

Electrical methods have also been used to detect the π^+-mesons produced in photon-nucleus collisions; these methods take advantage of the $\pi^+ \rightarrow \mu^+ \rightarrow e^+$ sequence of decays. Thus, Steinberger & Bishop (5) using the Berkeley synchrotron, have studied the π^+-mesons produced in a carbon target in the energy range 35 to 105 M.e.v. and in the angular range 45°–135° and have, within statistical error, confirmed the photographic measurements. Mozley (6) has investigated the dependence on the atomic number of the π^+ cross section for two specific energies, namely, 42 ± 7 and 76 ± 6 M.e.v. at an angle of $90 \pm 8°$ in the laboratory system. He carried out his measurements on H, Li, Be, B, C, Al, Cu, Sn, and Tb with the results for the relative cross sections per proton in arbitrary units shown in Table III. These results were not corrected for the meson absorption in the target; if the cross section for meson interaction with nuclei were geometrical, which it appears to be (see

TABLE II

Angle (lab.)	π^-/π^+	Mean Energy (M.e.v)
45°	1.29 ± 0.22	70
90°	1.30 ± 0.12	56
135°	1.34 ± 0.20	54

below), the correction would be as large as 8 per cent at 42 M.e.v. and 25 per cent at 76 M.e.v. It should also be remarked that the statistics are poor for Sn and Pb. Despite these reservations, it is apparent that there is a large drop in yield in going from hydrogen to the light nuclei and a more gradual drop in moving up the periodic table to the heavier nuclei. The first drop can readily be explained in terms of the Pauli exclusion principle which reduces the number of final states otherwise allowed by the momentum and energy conservation laws to a group of identical Fermi particles [cf. Chew & Steinberger (7)]. The more gradual drop can be explained in terms of the interaction of the outgoing π^+-mesons with the nucleons in the nucleus (the energies are too high for the Coulomb barrier to be effective), the interaction

TABLE III

Element	H	Li	Be	B	C	Al	Cu	Sn	Pb
σ per proton at 42 M.e.v.	6.6	3.32	2.82	3.02	2.60	2.50	1.92	1.66	0.51
σ per proton at 76 M.e.v.	8.07	2.80	2.13	2.28	1.93	1.68	1.17	0.51	0.80

becoming more effective as the number of nucleons increases. It is easy to see that such an interaction leads approximately to an $A^{-1/3}$ behavior (A is the atomic weight) for the cross section per nucleon; this fits quite well with the numbers in Table III. Such an explanation gathers credence when it is realized that the total cross section for all processes for photon energies of several hundred M.e.v. is much smaller than geometrical so that an A behavior for the meson production cross section would be expected on a priori grounds.

Production of π°-mesons in photon-nucleus collisions.—One of the important accomplishments of 1950 in meson physics was the definite establishment of the existence of a neutral π-meson. Several experiments carried out in 1949 had already given strong hints of the existence of a neutral meson decaying very rapidly into γ-rays. In particular, the experiment by Bjorklund *et al.* (8) (to be discussed more fully below) with the proton beam of the Berkeley cyclotron in which they observed single high energy γ-rays from targets of beryllium and carbon had its most likely explanation in terms of a neutral meson decaying into two γ-rays. Also, the analysis of the R-star by Bradt *et al.* (9), a cosmic ray star produced by an α-particle of about 10^{12} electron volts, showed that large numbers of γ-rays were produced, comparable in number to the charged π-mesons, and were probably due to neutral π-mesons.

It was not until the observation of coincidences between γ-rays resulting

from photon-nucleus collisions, however, that the existence of a neutral π-meson was definitely established. Using the Berkeley synchrotron, Steinberger *et al.* (10) detected the γ-rays from the π°-meson with an apparatus consisting of two crystal telescopes operating in coincidence at a variable angle β between them; the plane of the two telescopes and the target formed a variable angle θ with respect to the incident photon direction. For a synchrotron energy of 330 M.e.v., the average kinetic energy of neutral π-mesons (assuming the same mass as charged π-mesons) coming from a target like beryllium is 50 to 60 M.e.v. for $\beta=\theta=90°$. Consequently, the two decay photons should each possess an energy of about 100 M.e.v. so that the coincidence counting rate of the two telescopes should reach a maximum for a quarter inch lead converter (i.e., materializer into electrons). Steinberger *et al.* (10) demonstrated that one-fourth-inch lead converters for both telescopes do indeed give the maximum counting rate, that both telescopes require converters, and that one-fourth-inch copper converters have approximately the same conversion efficiency as one-sixteenth-inch lead converters. All of these observations provided strong evidence for the photon character of the particles giving rise to the coincidences. The nuclear origin of the photons was demonstrated by the fact that the coincidence rate was only six times as large (at $\theta=\beta=90°$) for a lead nucleus as for beryllium rather than 400 times as great if the photons had a shower origin. Finally, Steinberger *et al.* (10) reduced the beam energy to 175 M.e.v. and observed that the counting rate went down by a factor of 50 compared to 330 M.e.v.; this steep excitation function is characteristic of a phenomenon with a threshold. The fact that γ-rays of about 100 M.e.v. energy, of non-Coulombic origin, and with a threshold close to that of charged π-meson production are observed is overwhelming evidence for the production of a neutral π-meson with a mass approximately equal to that of the charged π-meson.

When it is recognized that the γ-rays are due to neutral mesons, it is possible to interpret the measured coincidence counting rates as a function of β and θ in terms of energy spectra for the π°-mesons. This interpretation is simplified by the fact that the kinematics of the two-photon decay of a moving π°-meson strongly favors the emission of two photons of almost equal energy close to the minimum angle $\beta_{\min}$ (where $\beta_{\min}$ is equal to $2 \sin^{-1} (\mu_0 c^2/E_0)$ where E_0 is the total energy of the π°-meson including its rest energy, μ_0 is its rest mass and c is the velocity of light), which is permissible for the given energy E_0. With this in mind, Figure 2, which contains the experimental results for the coincidence γ-counting rates from a beryllium target, represents meson spectra; each β corresponds fairly uniquely to a specific meson energy which is so indicated. Comparison with the charged meson spectra observed from carbon (cf. Fig. 1) shows strong similarities. Apart from the similarity of the neutral and charged meson spectra, the π°-spectrum provides definitive evidence for two-photon decay since the expected angular distribution for decay into more than two photons does not show a valley for small β. While the π°-spectra from beryllium and the

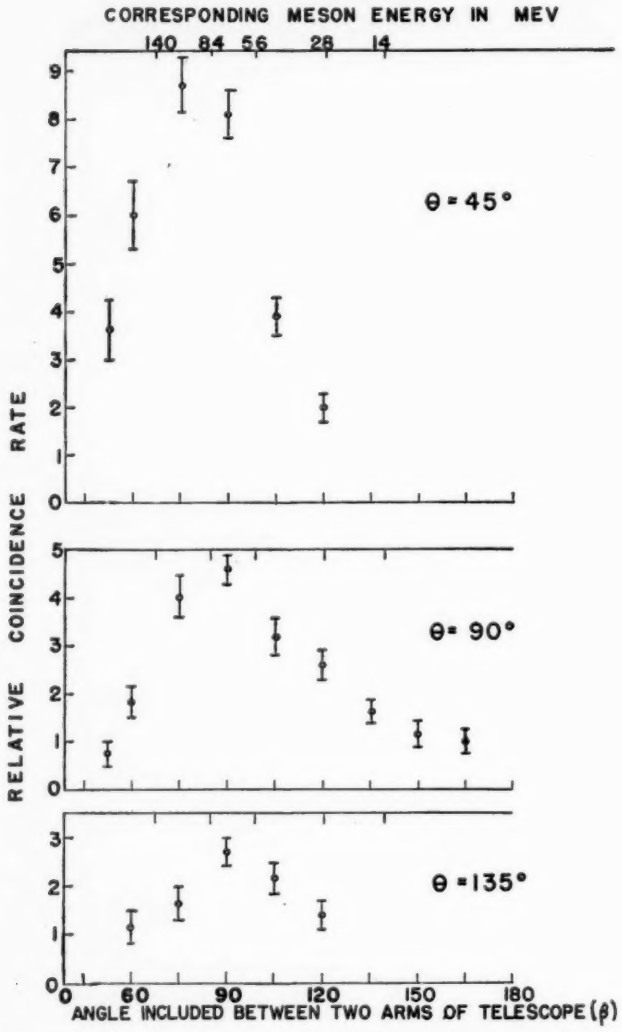
CORRESPONDING MESON ENERGY IN MEV
140 84 56 28 14
θ = 45°
θ = 90°
θ = 135°
RELATIVE COINCIDENCE RATE
0 60 90 120 150 180
ANGLE INCLUDED BETWEEN TWO ARMS OF TELESCOPE (β)

FIG. 2. Coincidence gamma counting rates (corresponding to π° spectra) from γ-rays on beryllium at three angles (peak photon energy -330 M.e.v.).

charged π-spectra from carbon are very comparable both as regards shape and magnitude, the relative cross section for π° production in hydrogen and carbon (at $\theta=\beta=90°$) turns out to be 0.12 ± 0.03 in contrast to a π^+ production ratio of about one-half. This difference is explicable, however, since π° production does not alter the isotropic number of the carbon nucleus whereas π^+ production does; the greater number of neutrons in the latter case leads, by virtue of the Pauli principle, to a greater reduction of the available phase

space than is the case for π^0 production. Preliminary measurements by the same authors on the relative yield per nucleon of 75 M.e.v. π^0's for nuclei heavier than carbon exhibit the same gradual fall-off as for π^+ production. If this is confirmed, it would imply a large interaction cross section of π^0-mesons with nuclear matter just as appears to be the case for π^+. This is one of the few methods available for measuring the interaction of π^0-mesons with nuclei because of their extremely short lifetime,—less than $5 \cdot 10^{-14}$ sec. (see below).

Production of charged π-mesons in photon-nucleon collisions.—Chronologically, the experiments on the production of π-mesons in photon-nucleus collisions came before similar experiments with hydrogen. The experiments with heavier nuclei have led to the establishment of the existence of the neutral π-meson and have permitted some indirect conclusions about the strength of the π-meson-nucleon interaction. In general, however, a study of π-meson production in heavy nuclei reveals more about the behavior of nucleons in nuclei than it does about the properties of the π-meson field and the character of the π-meson-nucleon interaction. The interactions among the nucleons in the nucleus are sufficiently strong so that for incident photon energies of several hundred M.e.v. (available with the high energy accelerators now in operation) it is these interactions which essentially determine the characteristic phenomena which are observed. On the other hand, experiments on π-meson production in photon-proton collisions (and presumably also in photon-deuteron collisions) should throw considerable light on the nature of the π-meson and its coupling with nucleons.

Experiments have been carried out on the photon production of π^+-mesons using liquid hydrogen and a *Bremsstrahlung* spectrum of 330 M.e.v. maximum energy [cf. Steinberger & Bishop (5)]. Figure 3 shows the measured energy spectrum of π^+-mesons produced at 90° with respect to the incident photon direction. The π^+-mesons are detected by an electrical method already mentioned in connection with carbon. The cross section per steradian at 90° as a function of photon energy is also shown in Figure 3, taking account of the *Bremsstrahlung* spectrum. The dotted curve shown is the excitation function which results if it is assumed that the π^+-meson has an interaction cross section equal to the nuclear area, as it seems to have (see below). The observed angular distribution of mesons produced by 250 M.e.v. photons is shown in Figure 4. For all these curves the absolute scale is uncertain by a factor 1.5, although the relative number, according to the authors, should be correct to within the statistical accuracy shown.

Comparison of the experimental results obtained thus far with the theoretical predictions based on either the weak coupling or classical theories [cf. Brueckner (4), Serber (11)] provides evidence against a scalar or vector field for the charged π-meson. The angular distribution of the π^+-mesons at the photon energy of 250 M.e.v. (cf. Fig. 4) is essentially isotropic and is therefore consistent with the pseudoscalar or pseudovector fields for the π^+-meson but in definite disagreement with the scalar and vector fields. The angular

distribution predicted by the scalar theory shows the characteristic dipole behavior distorted by the retardation term associated with the interaction of the charged meson with the photon. On the other hand, in the case of the pseudoscalar field, the photon is strongly coupled to the spin of the nucleon and the predicted angular distribution is reasonably isotropic. For the spin 1 theories (vector and pseudovector), the interaction of the photon with the meson dominates in both cases, but in the former case yields a

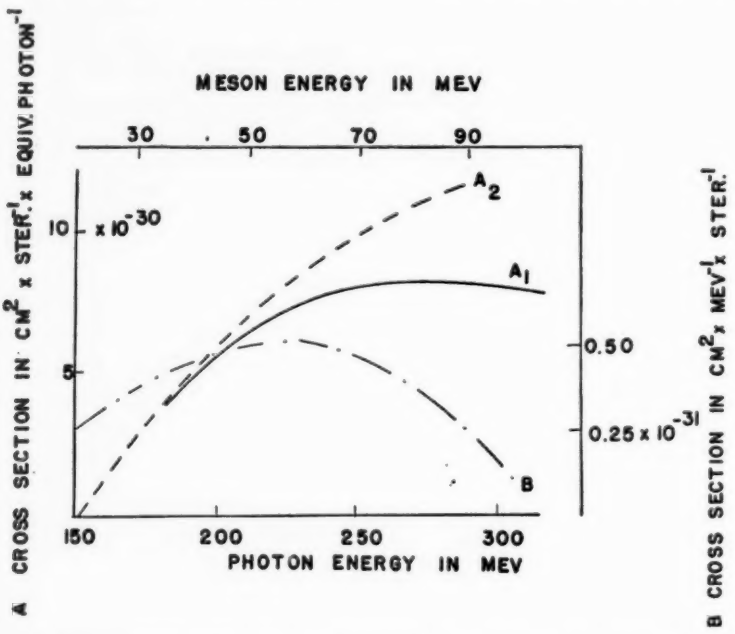

FIG. 3. A_1-excitation function for π^+-mesons from γ-rays on hydrogen at 90° without correcting for nuclear interaction of π^+-mesons. A_2-same as A_1 with correction for nuclear interaction. B. π^+ energy spectrum at 90° (peak photon energy = 330 M.e.v.).

strong forward maximum whereas in the latter it leads to a fairly isotropic angular distribution. The excitation curve at 90° with respect to the photon beam direction (cf. Fig. 3) does not decide between the pseudoscalar and pseudovector fields in view of the uncertainty of the interaction cross section of π^+-mesons in the energy region under consideration and the error of the measurements. When more extensive excitation measurements are available and when knowledge of the π^+-meson interaction cross section is pinned down, a decision between the pseudoscalar and pseudovector fields should be possible on the basis of these experiments. If the curve in Figure 4 is integrated over all angles, one arrives at a value of $1.5 \cdot 10^{-28}$ cm.^{2} for the total cross section for the production of π^+-mesons at a photon energy of 250

M.e.v. This value should be correct to better than a factor 2. This is a rather large cross section and is two or three times as large as the cross section per proton in a nucleus like carbon (see above).

Production of π°-mesons in photon-nucleon collisions.—Some measurements have been made of the production of π°-mesons in photon-proton collisions using the coincidence method described earlier. These measurements were carried out by Panofsky and co-workers (12) who find that the cross section is about one-third of the charged meson cross section at 250 M.e.v. and that the differential cross section at 45° is about twice that at 90°. A much more rapid excitation function for π° production is observed than for π^+ production. A straight-forward application of either spin 0 theory (scalar or pseudoscalar)—the π°-meson must possess spin 0 since it decays into two

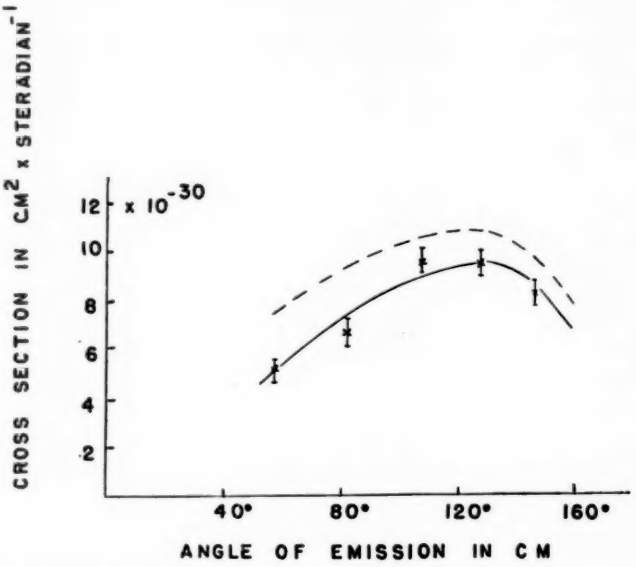

FIG. 4. Angular distribution of π^+-mesons from γ-rays on hydrogen at 250 M.e.v. without and with interaction (dotted curve).

γ-rays [cf. Yang (13)]—predicts a much smaller cross section (down by a factor $(\mu/M)^2$)[1] for π° production than for π^+ production if the anomalous magnetic moment of the proton is not taken into account. Kaplon (14) has shown that if a Pauli-type term is included in the Hamiltonian to represent the interaction of an electromagnetic field with the anomalous magnetic moment of the proton, roughly equal values for the neutral and charged π-meson coupling constants will fit the experimental data for the pseudoscalar theory; in the scalar theory, the discrepancy is accentuated. Moreover,

[1] μ and M are the meson and nucleon masses respectively.

the theoretical excitation function and angular distribution are in reasonable accord with experiment. It thus appears that the π^0-mesons as well as the π^+-mesons produced in photon-proton collisions have a magnetic origin. The magnetic moment explanation of π^0 production can be checked by performing experiments with deuterium since the neutron can only interact through its anomalous magnetic moment and a π^0-meson cannot carry a magnetic moment at all (since it possesses spin 0).

Nucleonic Production of π-Mesons

Production of charged π-mesons in nucleon-nucleus collisions.—Just as in the case of the photonic production of π-mesons, the nucleonic production was first studied in nuclei heavier than the proton. For nucleonic production,

TABLE IV

Proton Energy	345	306	269	233	201	167
Relative Yield	100	47	22	8	1	0

there was good reason for starting with heavier nuclei since the threshold energy is pushed down from about 2 μc^2 for a proton to about μc^2 for the heavier nucleus (because of the momentum distribution of the nucleons in the target nucleus). McMillan & Teller (15) first emphasized this point and showed that above threshold, the meson production cross section in nucleon-nucleus collisions should show a rapid increase with the incident energy of the nucleon. This contrasts with the photonic production of mesons where the threshold is close to μc^2 for a free nucleon and is changed only slightly by the presence of the additional nucleons. Thus, in photon-nucleus collisions, the cross section should not vary as rapidly in the neighborhood of μc^2 as the cross section in nucleon-nucleus collisions.

Some early measurements by Jones & White (16), using photographic methods, confirm the rapid variation of the π^--meson excitation function. Table IV contains their results for π^--mesons in the energy region 2 to 10 M.e.v. emitted within an angle of 45° with respect to the incident proton beam. The numbers in Table IV can be fitted, within the experimental accuracy, with the quadratic function which the Fermi gas model would lead one to expect [cf. McMillan & Teller (15)]. Richman & Wilcox (17), using the Berkeley cyclotron, have measured photographically the differential cross section for both π^+ and π^- production from a carbon target at 345 M.e.v. and at an angle of $90 \pm 12°$ with respect to the incident proton beam. Their results are shown in Figure 5.[2] The integrals of the two curves over the meson energy yield $2.0 \pm 0.5 \cdot 10^{-28}$ cm.^{2}/steradian per nucleus for π^+-meson production and

[2] They are uncorrected for the nuclear interaction of the mesons in the absorber which depresses the total cross section by at most 25 per cent.

$4.0 \pm 1.6 \cdot 10^{-29}$ cm.²/steradian per nucleus for π^--meson production. Weissbluth (18) has carried out similar measurements for lead and his results are given in Figure 6. The integrals of the two curves over the meson energy are $6.0 \pm 1.1 \cdot 10^{-28}$ cm.²/steradian for π^+ production and $4.3 \pm 1.8 \times 10^{-28}$

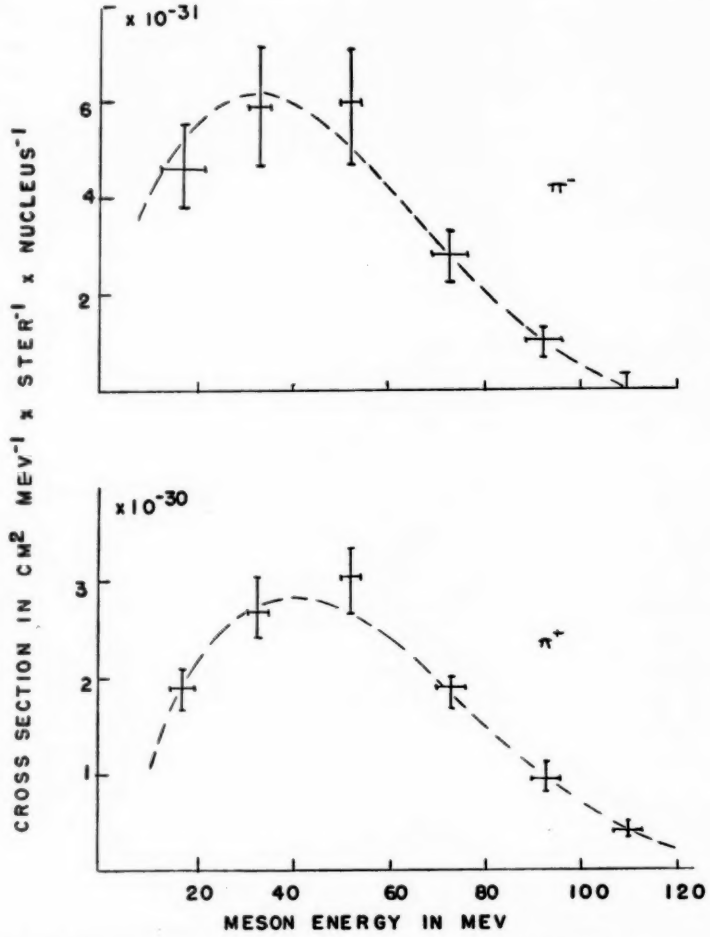

FIG. 5. $\pi^{\pm}$ Energy spectra from protons on carbon at 90° (345 M.e.v. protons).

cm.²/steradian for π^- production. There are several interesting points which emerge from a comparison of the meson spectra obtained from carbon and lead. It is observed that the cut-off energy is higher for π^+ production than for π^- production for both carbon and lead and is presumably due to the Pauli principle which makes the production of π^- less favorable than π^+, especially at the high energy end. The suppression of low energy π^+-mesons

and the enhancement of π^--meson production in lead compared to carbon is presumed to be attributable to the Coulomb field of the nucleus as is also the increase in energy at which the maximum in the cross section occurs for π^+ production compared to π^- production. Another point of comparison which follows from Figures 5 and 6 is the π^+/π^- ratio; if one restricts oneself to energies greater than 40 M.e.v. (so that the Coulomb effect ceases to exert its influence), the a priori π^+/π^- ratio would be $(A+Z)/(A-Z)$, assuming equal cross sections for π^+ and π^- production. The marked deviations from

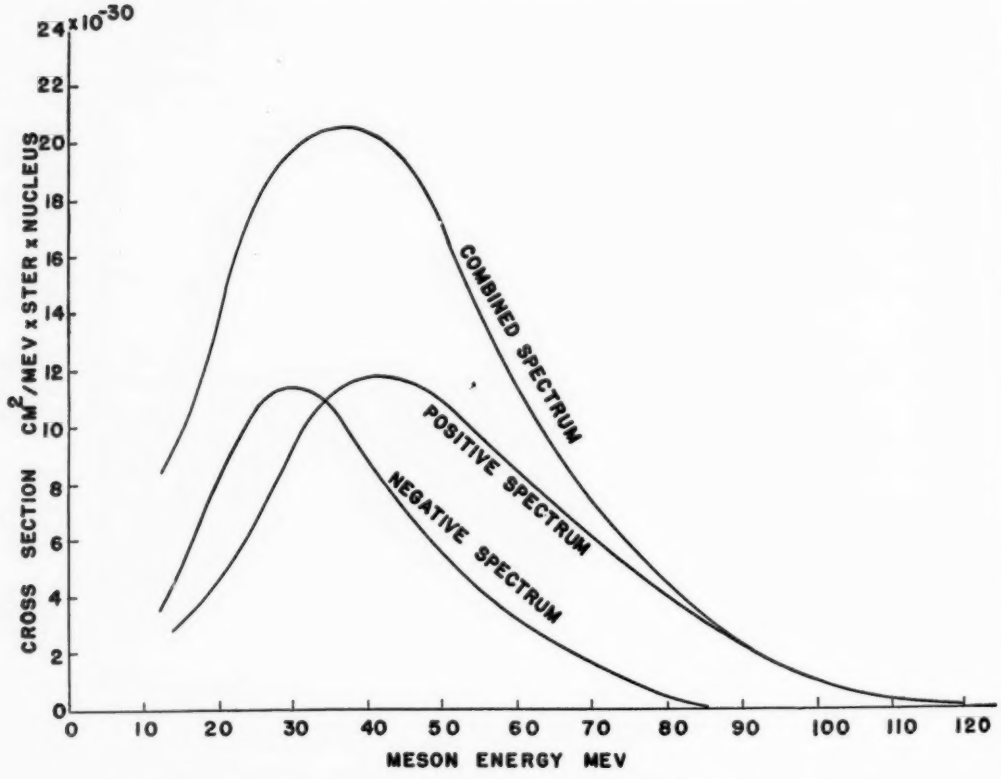

FIG. 6. $\pi^{\pm}$ Energy spectra from protons on lead at 90° (345 M.e.v. protons).

this ratio, especially in carbon, is presumed to be due to the operation of the Pauli principle already cited above [cf. Chew & Steinberger (7)].

In order to determine whether the π^+/π^- ratio is reversed in favor of π^--mesons when the incident nucleon is a neutron, Bradner *et al.* (19) studied the numbers of π^-- and π^+-mesons in the energy range 50 to 65 M.e.v. produced by the 280 M.e.v.—centered neutron beam resulting from 340 M.e.v. protons impinging on a carbon target. The mesons were observed at 90° with

respect to the incident neutron beam. The π^-/π^+ ratio was found to be 12.6 ± 1.5 compared to a π^+/π^- ratio of 5 at 90° for 345 M.e.v. protons striking carbon. This strikingly different result is in accord with theoretical expectation which predicts for energetic mesons (far above the Coulomb barrier) produced by incident neutrons the π^-/π^+ ratio $(2A-Z)/Z$ multiplied by an enhancement factor which is greater at 280 M.e.v. than at 345 M.e.v.

Clark (20) has measured by electrical means the π^+ and π^- yields as a function of atomic number for 40 M.e.v. mesons produced by the 240 M.e.v. protons from the Rochester cyclotron; his results are essentially similar to the photonic production measurements of Mozley (6).

Camerini *et al.* (21) have measured the charged π-meson energy spectrum resulting from proton-nuclei collisions in photographic emulsions; by combining scattering and grain density measurements they were able to discriminate between π-mesons and protons for energies up to 1,500 M.e.v. In this energy range, they found a differential energy spectrum which can be represented by $dE/E^{1.5}$ where E is the total energy of the π-meson (including its rest mass). This spectrum was also deduced by Sands (22) as a result of a careful analysis of the intensity of μ-mesons in the cosmic radiation as a function of altitude and the energy spectrum of μ-mesons at sea level.

Production of π°-mesons in nucleon-nuclei collisions.—We have already remarked that the first conclusive demonstration of the existence of the π°-meson was provided by the observation of coincidences between γ-rays resulting from the collision of photons with the nuclei of beryllium and carbon. However, we have also pointed out that the first experiment with high energy accelerators which provided very strong evidence for the existence of π°-mesons was carried out by Bjorklund *et al.* (8) with the proton beam of the Berkeley cyclotron. These authors observed single high energy γ-rays resulting from the collision of protons with targets of beryllium and carbon and, by varying many different parameters, were able to establish powerful arguments for the production of π°-mesons. In view of the intrinsic interest of the experiment and its historical importance, we shall present the results and outline the arguments.

Bjorklund *et al.* (8) observed the γ-rays in approximately the forward and backward directions with respect to the proton beam for proton energies ranging from 180 to 340 M.e.v. After establishing that the radiation actually consisted of photons by performing attenuation measurements in lead and aluminum, the Berkeley group measured the γ-ray spectra with a pair spectrometer. In this manner, using a carbon target, they obtained the γ-ray curves shown in Figures 7 and 8 for the forward and backward directions respectively. It is seen that the cross section varies by a factor of about a hundred in the energy region under consideration.

The Berkeley group was also able to obtain absolute cross sections for the production of photons by a carbon nucleus. These results are shown in Table V. Finally, they measured the γ-ray yield from a carbon target for 340 M.e.v. protons for four different angles and the results are shown in Figure 9.

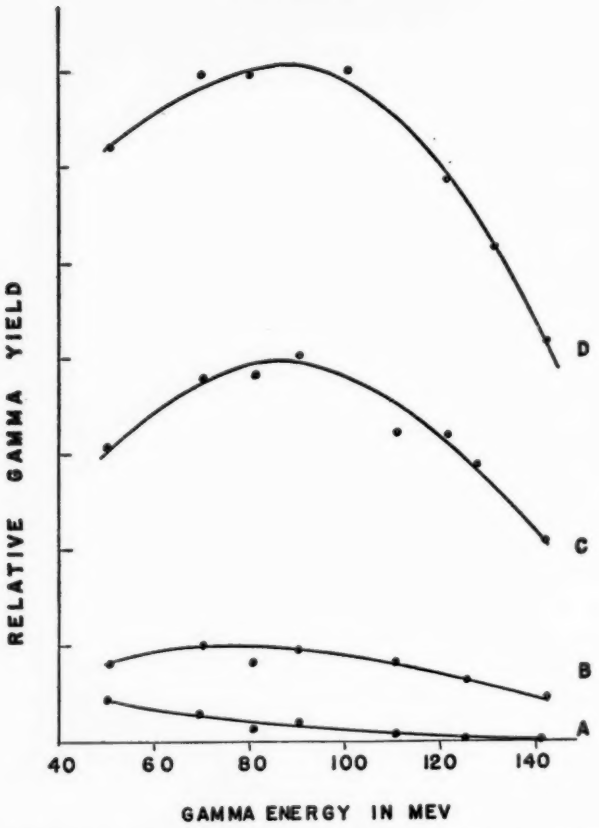

FIG. 7. γ-Ray spectra from protons on carbon in forward direction at four proton energies: A—180 M.e.v., B—230 M.e.v., C—290 M.e.v., D—340 M.e.v.

TABLE V

	lab system	$\beta=0.32$ system
$d\sigma(0°)$ at peak	$1.2\cdot10^{-30}$	$0.85\cdot10^{-30}$
$d\sigma(0°)$ at peak	$0.6\cdot10^{-30}$	$0.85\cdot10^{-30}$
$\sigma(0°)$	$1.5\cdot10^{-28}$	$0.75\cdot10^{-28}$
$\sigma(180°)$	$0.35\cdot10^{-28}$	$0.75\cdot10^{-28}$
σ_{tot} (assuming isotropy in the center of mass system)	—	$1\cdot10^{-27}$

If photons are emitted with spherical symmetry in some coordinate system moving with velocity βc, and if the spectrum of photons in that system is $I_c(E)$, then the spectrum in the laboratory system at an angle θ will be

$$I(E,\theta) = \frac{\sqrt{1-\beta^2}}{1-\beta\cos\theta} I_c\left(\frac{1-\beta\cos\theta}{\sqrt{1-\beta^2}} E\right)$$

where the Doppler shift and aberration effects have been taken into account. If this formula is used to transform the four 340 M.e.v. curves of Figure 9

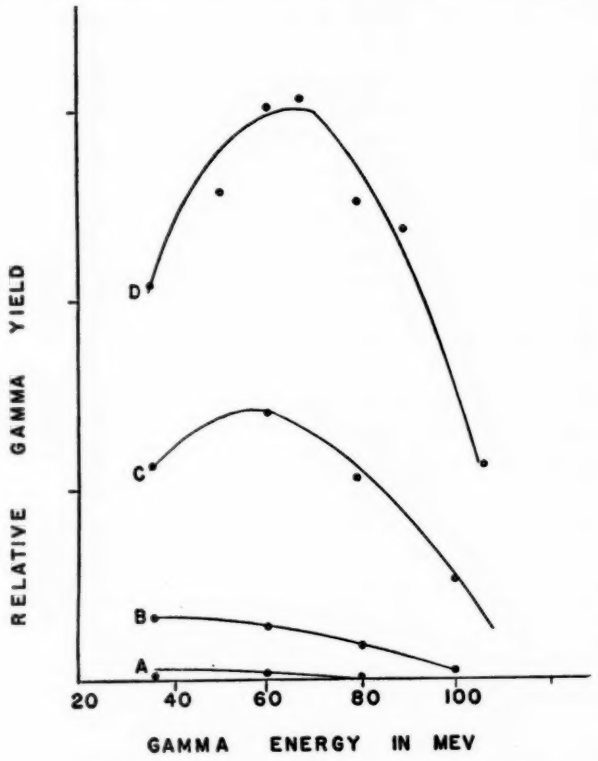

FIG. 8. Same as Fig. 7 in backward direction.

to a system moving with $\beta=0.32$, one obtains a single consistent curve (within the experimental accuracy). The value $\beta=0.32$ is a reasonable choice for the center of mass system of the colliding proton and the target nucleus for the following reason: a 340 M.e.v. proton has a β of 0.67 and the β of the center of mass of such a proton and a stationary nucleon would be 0.39. However, if, as Figures 7 and 8 indicate, the production process for photons is highly energy dependent, the major contribution to the cross section should come from nucleons moving with maximum velocity in the nucleus ($\approx$25 M.e.v.) and in an approximately opposite direction to the incident proton. For such a choice of numbers the center of mass velocity is in the range 0.3 to 0.35.

On the basis of these data, it is possible to rule out almost all explanations

for the origin of the γ-rays except the neutral meson hypothesis. Thus, on the basis of the large Doppler shift observed in the experiment, the possibility of nuclear excitation or isobaric states of nucleons can be ruled out. On the basis of the observed γ-ray threshold in the neighborhood of 175 to 200 M.e.v., the hypothesis of excited states of a π meson being responsible for the radiation can be eliminated. Finally, a nuclear *Bremsstrahlung* origin of the γ-radiation

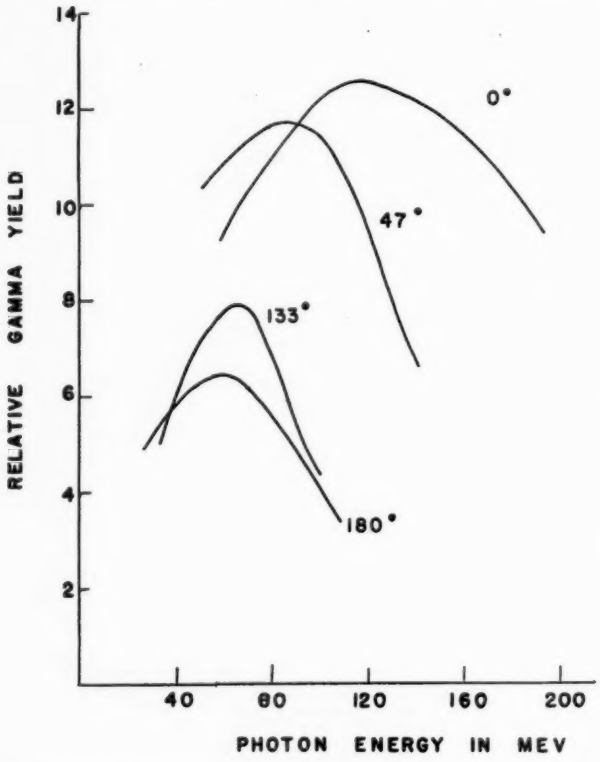

FIG. 9. γ-Ray spectra from protons on carbon at four angles (340 M.e.v.).

can be ruled out because of the observed rapid rise of yield with energy. No reasonable theory of nuclear *Bremsstrahlung* γ-rays predicts the extremely rapid increase of yield which is observed [cf. Ashkin & Marshak (23) and Simon (24)].

In contrast, the neutral meson hypothesis fits all of the data extremely well. Thus, the excitation function for the production of the high energy γ-rays is very similar to the excitation function for charged π production and both can be understood in terms of the momentum distribution of the nucleons in the target nucleus. Furthermore, the absolute yield of γ-rays is close to that for charged π-mesons produced in proton-nucleus collisions. The occurrence of a threshold for the γ-radiation at about 175 M.e.v. and the

peak of the radiation at 75 M.e.v. in the center of mass system is consistent with the two-photon decay of the neutral meson. The fact that the threshold is about at the same energy as for charged π production and the observation that the γ-ray peak in the center of mass system occurs at the same point (75 M.e.v.), independent of the incident proton energy, both are in accord with a neutral meson origin of the γ-rays. Theoretical calculations of the expected γ-ray energy spectra on the two-photon hypothesis, assuming that the decay is isotropic in the rest system of the neutral meson, fit the experimental curves extremely well. A mass of the π°-meson of about 150 M.e.v. is consistent with this experiment.

During 1950, many cosmic ray experiments on penetrating and Auger showers were performed, from which the production of π°-mesons in nucleon-nucleus collisions could be inferred. Thus, cloud chamber experiments [e.g., Gregory *et al.* (25)], in which electronic cascade showers are observed to accompany penetrating showers, find their most natural interpretation in terms of a simultaneous production of neutral and charged π-mesons; the neutral mesons decay very rapidly into γ-rays which in turn initiate a soft component cascade. Also, counter observations of the large extensive air showers (Auger showers) with which are associated a large number of penetrating particles (e.g., Cocconi & Tongiorgi (26)] can be explained in terms of a highly multiple production of neutral and charged π-mesons in the high atmosphere by the protons and heavy nuclei of the primary cosmic radiation. This explanation seems reasonable even though the degree of multiplicity, the initial energy spectra of the charged and neutral π-mesons, and the manner in which the penetrating component propagates are not clearly understood.

However, the most conclusive cosmic ray evidence for the production of π°-mesons in nucleon-nuclei collisions has been obtained with photographic methods by Carlson *et al.* (27). These authors have measured the energies of 500 electron pairs—presumed to be produced by γ-rays—in plates exposed at 70,000 ft. The energy spectrum of the γ-rays deduced from these measurements is shown in Figure 10. Since π°-mesons with a given energy E_0 (including the rest mass) would yield a square pulse of γ-rays with energy between

$$\frac{E_o - cp_o}{2} \quad \text{and} \quad \frac{E_o + cp_o}{2} \quad (cp_o = \sqrt{E_o^2 - \mu_o^2 c^4})$$

if the mesons are produced isotropically in the neighborhood of the plates and the two decay γ-rays are emitted isotropically in the rest system of the π°-meson, it follows that the minimum and maximum energies of the γ-rays, $E_{\min}$ and $E_{\max}$ will obey the relation $\sqrt{E_{\min} E_{\max}} = \mu_0 c^2/2$ for each given energy E_0. Consequently, if F (E) dE is the differential energy spectrum of π°-mesons produced by the primary cosmic rays (chiefly protons) interacting with the air nuclei, it can easily be shown that the observed γ-ray spectrum $N(E)$ will be related to $F(E)$ by means of the relation:

$$N(E) = \int_{E + \frac{\mu_o^2 c^4}{4E}}^{\infty} \frac{F(E')\mathrm{d}E'}{\sqrt{E'^2 - \mu_o^2 c^4}}.$$

Clearly, the peak of the distribution function $F(E)$ will occur when $E_{\min}$ is equal to $E_{\max}$ or $E_{\text{peak}}=\mu_0 c^2/2$. From the observed peak, Carlson *et al.* (27) derive the mass of the π°-meson, which turns out to be 295 ± 20 electron masses, and from the observed distribution function $N(E)$, they derive the production spectrum $F(E)dE=dE/E^{1.5}$. The spectrum agrees with the charged π-meson spectrum observed in cosmic ray nucleon-nuclei collisions at the same altitude (see above).

Production of charged π-mesons in nucleon-nucleon collisions.—Just as in the case of photonic production of π-mesons, nucleonic production begins to shed a clearer light on the nature of the π-meson and its nucleon coupling

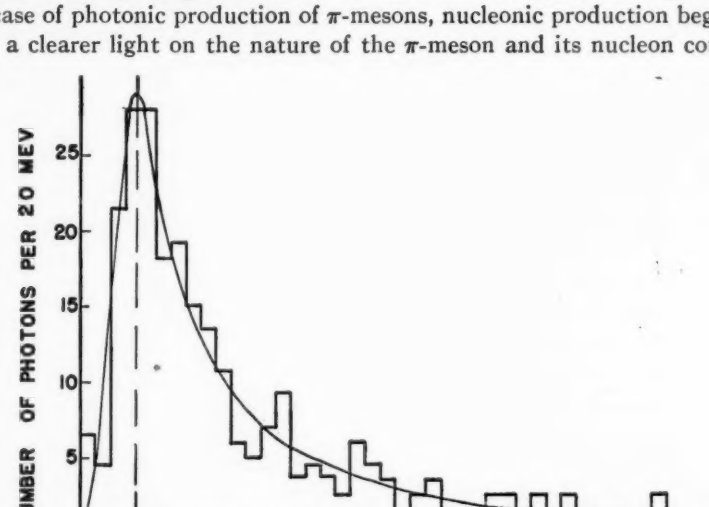

FIG. 10. γ-Ray spectrum in photographic emulsions at 70,000 ft.

when the target nucleus is the bare proton. The only nucleon-nucleon experiments which have been carried out thus far have dealt with the production of π^+- and π°-mesons in proton-proton collisions. Two different experiments have been performed on the π^+ production in proton-proton collisions: one by Cartwright *et al.* (28) using a subtraction technique (subtracting the π^+ production in proton-carbon collisions from the corresponding numbers in proton-polyethylene collisions) and the second by Peterson (29) using liquid hydrogen. In both experiments, the π^+-mesons were detected in photographic plates and the incident proton energy was 340 M.e.v. The largest cross section is observed in the forward direction and the measured π^+-energy spectrum in this direction is shown in Figure 11. The two experiments by Cartwright *et al.* (28) and by Peterson (29) have together led to the cross section/steradian shown in Table VI. The enormous high energy peak in the π^+-spectrum (cf. Fig. 11) cannot be explained in terms of any of the existing

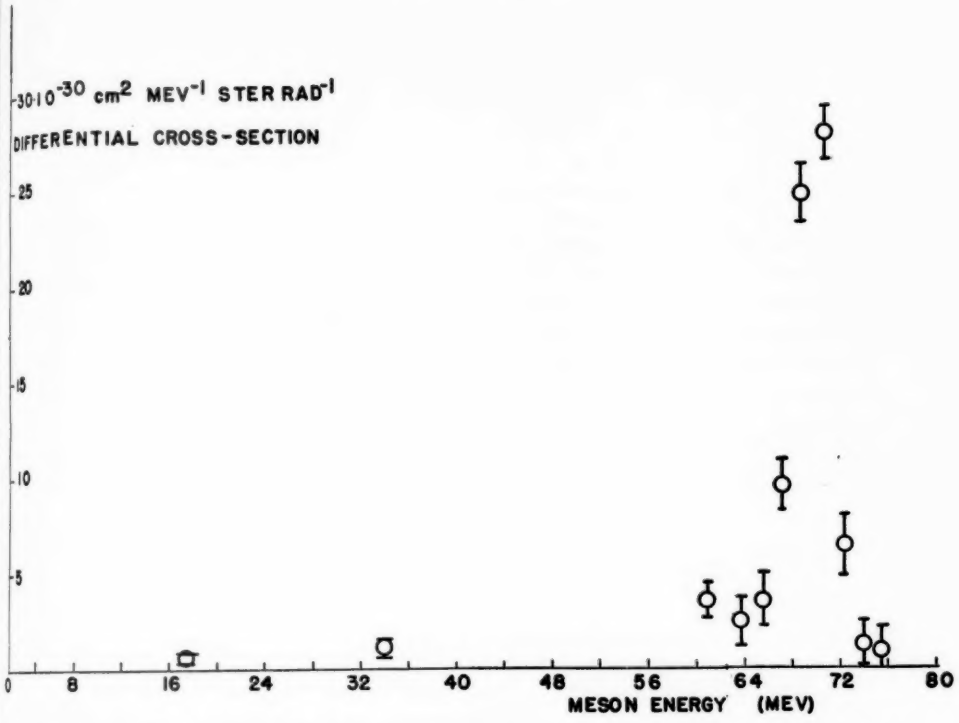

FIG. 11. π^+ Energy spectrum from protons on hydrogen in forward direction (340 M.e.v.).

theories for the production mechanism: $P+P \rightarrow \pi^+ + N + P$ even when account is taken of the strong neutron-proton interaction in the final state. It must be presumed that the peak is associated with the reaction: $P+P \rightarrow \pi^+ + D$ which leads to a discrete π^+-spectrum (displaced towards the high energy end by 2 to 4 M.e.v.) which cannot be resolved from the upper end of the continuous spectrum resulting from the reaction: $P+P \rightarrow \pi^+ + N + P$. This interpretation has been confirmed by recent observations of coincidences between π^+-mesons and deuterons [Crawford *et al.* (30)] and it is probable that one-half to two-thirds of the cross sections listed in Table VI are due to the former reaction. The numbers listed in Table VI fit very closely a $\cos^2\theta$ distribution in the center of mass system.

TABLE VI

Lab angle	0°	18°	30°	60°
$d\sigma/d\Omega$ (in units of 10^{-28} cm.^{2})	2.00	1.63	0.58	0.08

An experiment on the production of π°-mesons in proton-proton collision [Crandall *et al.* (31)] has also been performed; γ-rays have been looked for along the lines of the Bjorklund *et al.* (8) experiment and have not been observed. The negative result obtained enables one to set an upper limit of 1 per cent of the cross section for the production of π^+-mesons in proton-carbon collisions.

As regards the theoretical situation, it can be stated at once that the theoretical conclusions drawn from the nucleonic production experiments are consistent with the ones implied by the photon-proton experiments, namely that the neutral π-meson possesses spin 0 and odd parity (pseudoscalar) and the charged π-meson spin 0 and odd parity (pseudoscalar) or spin 1 and even parity (pseudovector). We have used the term consistent because the theoretical predictions for the production of mesons in nucleon-nucleon collisions are even less trustworthy than those for the production of mesons in photon-nucleon collisions. This is true for several reasons: the photon-nucleon production of mesons is a first order process in the meson coupling constant in contrast to the nucleon-nucleon production which is a third order process if a consistent field-theoretic viewpoint is adopted. (It is possible to treat π-meson production as a first order process if the nucleon-nucleon scattering is represented phenomenologically rather than field-theoretically; however, one's ignorance of the nuclear force is a serious handicap to this treatment.) This implies that a field-theoretic calculation of π-meson production in nucleon-nucleon collisions requires some assumption to be made regarding the kinds of virtual mesons which are responsible for the nucleon-nucleon interaction. Clearly, it matters whether the nucleon-nucleon interaction is ascribed to π-mesons alone or whether it is assumed that several kinds of meson fields (of different masses, etc.) contribute to the nuclear interaction. In lowest order, the photon-nucleon production of π-mesons only involves the π-meson field and this is a great advantage if the higher order radiative corrections are not too important which they probably are not in the non-relativistic energy region under consideration. Moreover, one can carry out a classical calculation of the photonic production process which agrees well with the weak coupling perturbation theory whereas the best one can do with the nucleonic production is to compute the cross sections phenomenologically subject to the uncertainties mentioned above. Despite all these qualifications, the fact that the pseudoscalar π-meson field (with pseudovector coupling to the nucleons) can explain both the $\cos^2\theta$ angular distribution for the π^+ production and the marked reduction in the π° cross section in like-nucleon collisions may be significant after all [cf. Brueckner (32) and Kaplon (33)].

Properties of π-Mesons

In the sections on Photonic Production of π-Mesons and Nucleonic Production of π-Mesons, we have discussed the two fundamental mechanisms for the production of π-mesons: photon-nucleon collisions and nucleon-

nucleon collisions. A comparison of the theoretical predictions with the existing experimental data permitted certain deductions concerning the properties of the charged and neutral π-mesons. In this section, we consider in somewhat more detail the properties of the π-mesons: the most accurate mass and life-time determinations of both the charged and neutral mesons, their modes of decay, and the various experiments bearing on the determination of their spins and parities. We shall, as before, devote our chief attention to experiments with artificially produced π-mesons although the corroborative evidence furnished by cosmic ray experiments will be mentioned wherever possible.

Masses of the π-mesons.—Powell, in his review article on "Mesons" (34), has discussed at some length the different methods for determining the mass of the charged π-meson (and the charged μ-meson for that matter) with photographic emulsions. We shall not repeat this discussion here except to remark that it is necessary to measure two parameters in order to determine the meson mass, namely two of the following: the radius of curvature in a magnetic field, the range, the grain density or the multiple Coulomb scattering. The best determination of the π^+- and π^--meson masses based on these methods has led to the values $m_{\pi^+}=277.4\pm1.1$ and $m_{\pi^-}=276.3\pm1.3$ electron masses [derived from measurements of the curvatures and ranges—Barkas *et al.* (35)]. During 1950, two accurate determinations of the charged π-meson mass have come from somewhat unexpected directions. The first measurement has followed from a study of the slow meson reaction: $\pi^-+P\rightarrow N+\gamma$, in which the energy of the discrete γ-ray is measured. Since the π^--meson is absorbed from the K-shell of the mesic hydrogen atom, where the binding is only 3 kv., it can be assumed that the π^--meson is at rest and hence the mass of the π-meson is simply related to the γ-ray energy. The energy of the γ-ray has been measured with a pair spectrometer [Panofsky *et al.* (36)] and when proper account is taken of the resolving power of the pair spectrometer, the mass of the π^--meson turns out to be 275.2 ± 2.5 electron masses. The other accurate determination has been made possible by taking advantage of the fact that the reaction: $P+P\rightarrow\pi^++D$ leads to a discrete π^+-meson energy which can be taken as the peak of the π^+-meson spectrum (cf. Fig. 11). From this peak and an accurate knowledge of the incident proton energy, the value 275.1 ± 2.5 electron masses has been deduced [Cartwright (37)].

The mass of the π°-meson can only be determined indirectly because it decays into two γ-rays with such an extremely short lifetime. The experiments on the production of π°-mesons (compare above) have provided rough evidence for a mass about equal to that of the charged π-meson, namely in the neighborhood of 300 electron masses. A somewhat better measurement of the π°-mass has also been cited, namely the experiment of Carlson *et al.* (27), in which the π°-mass is deduced from the measured γ-ray spectrum at 70,000 ft. However, the most accurate determination of the π°-meson mass was made possible by the fact that it is smaller than the π^--meson mass by

at least 1.25 M.e.v. With a $\pi^- - \pi^\circ$ mass difference greater than 1.25 M.e.v., the slow meson reaction (a): $\pi^- + P \rightarrow N + \pi^\circ$ can compete with the reaction (b): $\pi^- + P \rightarrow N + \gamma$ already mentioned in connection with the π^- mass. Reaction (a) has been measured with the same apparatus as reaction (b) since the π° quickly decays into two γ-rays. The measured γ-ray spectrum should be a square pulse assuming, as usual, that the π°-meson emits its two γ-rays isotropically in its own frame of reference; the experimental curve is shown in Figure 12 [taken from Panofsky *et al.* (36)] as is also the γ-ray emitted in

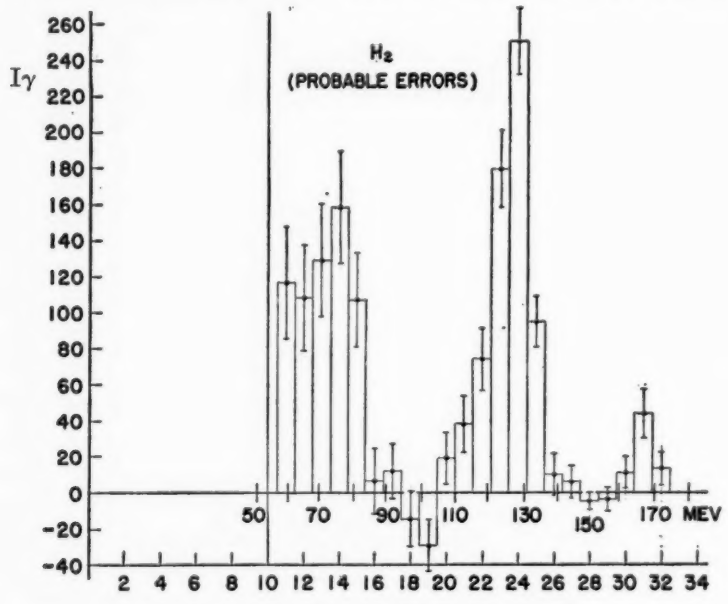

FIG. 12. γ-Ray spectrum from $\pi-$ on hydrogen.

reaction (b). The lower and upper spectral limits turn out to be 53.6 M.e.v. and 85.0 M.e.v. respectively and this leads to a $\pi^- - \pi^\circ$ mass difference of 10.6 ± 2.0 electron masses. If the value 275.2 ± 2.5 electron masses is chosen for the π^--meson, the value 264.6 ± 3.2 electron masses follows for the π°-meson mass. This remarkably accurate determination of the π°-meson mass is, of course, due to the Doppler amplification of the small mass difference between π^- and π°—about 5 M.e.v.—into a large energy spread for the γ-rays—about 30 M.e.v.

Decay of the π-mesons.—The charged π-meson is an unstable particle which decays much faster (by a factor of about 100) than the lighter μ-meson. Actually, the μ-meson is the decay product of the π-meson and it has been possible to observe the sequence of decays $\pi^+ \rightarrow \mu^+ \rightarrow e^+$ in a photographic plate. It was this sequence of decays, too, which was used to detect π^+-mesons electrically in the production experiments with photons. Thus far, no

conclusive experimental evidence exists for the direct decay of the π-meson into an electron; actually, Friedman & Rainwater (38) have shown that not more than one π-meson in 1,400 decays into an electron. Let us then examine the experimental evidence bearing on the lifetime for π-μ decay and on the decay products resulting from this reaction.

Some cosmic ray experiments, such as the difference in upward and downward flux of π-mesons [Camerini *et al.* (39)] and variation of the intensity of μ-mesons as a function of the underground depth [cf. Greisen (40)], have led to rough values for the lifetime of the π-meson of the order of 10^{-8} sec. However, it is clear that, in principle, the most accurate measurement of the π-μ lifetime will be made with artificially produced π-mesons. Unfortunately, the agreement among different measurements was at first none too good, although more recently the experiments seem to be settling down to a value of about 2.5 to $2.6 \cdot 10^{-8}$ sec. for the mean lifetime. The first accelerator experiment on the lifetime was carried out by Richardson (41), who measured the number of π^--mesons produced in proton-carbon collisions as a function of angular distance in the magnetic field of the Berkeley cyclotron. The π^--mesons were detected by photographic plates placed at various path lengths from the target inside the cyclotron vacuum tank. Richardson found the mean life to be $\tau^- = 1.11 \times 10^{-8}$ sec. By the same method, Martinelli & Panofsky (42) measured the mean life of the π-meson as $\tau^+ = 1.97 \times 10^{-8}$ sec. During 1950 several electronic measurements of the π^+ lifetime were made, taking advantage of the time lag between the two bursts of fluorescence resulting from π-μ decay and μ-electron decay in the same scintillation crystal to identify the π-μ decay process. The distribution in time of the first burst allows a measurement of the π^+ lifetime. A measurement of this type by the Massachusetts Institute of Technology group [Kraushaar *et al.* (43)], using π^+-mesons produced in carbon or beryllium targets by the γ-rays from the Massachusetts Institute of Technology synchrotron led to a mean life of $1.65 \pm 0.33 \cdot 10^{-8}$ sec. However, this value is based on poor statistics (only 57 events) and a similar measurement carried out at the same time at Berkeley led to a more reliable value [Chamberlain *et al.* (44)]. On the basis of an analysis of 1,277 events, the Berkeley group obtained the value $\tau^+ = 2.60 \pm 0.14 \cdot 10^{-8}$ sec. (averaging the differential and integral data). More recently, Jakobson *et al.* (45) have made an even more accurate measurement and the best value for the lifetime at the present time appears to be $2.54 \pm 0.11 \cdot 10^{-8}$ sec. It is worth remarking that this lifetime refers to the π^+-meson and it would be desirable to have an equally accurate measurement of the π^- lifetime. The best π^- lifetime measured thus far, by the Columbia group [Lederman *et al.* (46)] yields the value $2.9 \pm 0.3 \cdot 10^{-8}$ sec. This is much better than the Richardson value and points to the extremely probable result that the π^+ and π^- lifetimes are equal.

The π^+-meson is known to give rise to μ^+-meson at the end of its track in a photographic emulsion. As a matter of fact, it was this observation which led Lattes *et al.* (47) to the discovery of the charged π-meson. Since all avail-

able evidence [cf. Lattes *et al.* (48)] indicates that the μ^+-meson resulting from π^+ decay has a fixed range of about 600 μ in the photographic emulsion (6.14 ± 5 μ, to be exact, corresponding to an energy of 4.1 M.e.v.—the small deviations from the average, of the order of 5 per cent, are explicable in terms of straggling), there can only be one other neutral particle in addition to the μ-meson resulting from the decay of the π-meson. Unfortunately, slight errors in the range-energy calibration for the μ-meson and in the masses of the π- and μ-mesons lead to considerable uncertainty in the mass of the neutral particle and the upper limit on the mass of the neutral decay particle is at best several electron masses. It is simplest, of course, not to invoke a new type of neutral particle and to assume that the neutral decay particle possesses zero rest mass and is a photon or a neutrino. If there is a theoretical connection between π-μ decay and the absorption of μ-mesons by heavy nuclei [cf. Marshak & Bethe (49)], then the experiment by Piccioni (50) would argue against the neutral particle being a photon. A more recent experiment by O'Ceallaigh (51) to decide whether the neutral particle is a photon led to negative results. O'Ceallaigh carefully searched for electron pairs which would be produced by the 30.1 M.e.v. photon in a direction opposite to that of the decay μ-meson. In a total scan length of 38 cm. in the vicinity of 250 π-μ decays, not a single electron pair was found. Since, if a photon were emitted in the π-μ decay, the probability that it would fail to produce an electron pair is $4 \cdot 10^{-3}$ under the conditions of the experiment, the evidence is strong that the neutral particle accompanying the μ-meson in the π-meson decay is not a photon. It is therefore likely that the π-meson decays into a μ-meson and a neutrino.

We have already pointed out that the decay products of the π°-meson are two γ-rays which make it possible to detect the π°-meson because of its extremely short lifetime. As regards the measurements of the actual lifetime itself, the best measurement so far fixes the upper limit as $5 \cdot 10^{-14}$ sec. This result has been obtained by Carlson *et al.* (27) by observing the electron pairs produced by the photons associated with a star emitting shower particles. These authors surveyed the area in the vicinity of stars containing at least three shower particles and obtained a distribution of the perpendicular distances d from the lines passing through accompanying electron pairs. On the basis of this d distribution (derived from 15 electron pairs), an upper limit of $5 \cdot 10^{-14}$ sec. was deduced for the π° lifetime. This value of the π° lifetime is consistent with several earlier determinations of the same quantity. For example, the experiment of Bjorklund *et al.* (8) on the γ-rays arising from proton-nuclei collisions, which was taken as evidence for the production of π°-mesons, led to an upper limit on the π° lifetime of 10^{-11} sec. in virtue of the disappearance of the γ-rays when the target was moved behind a thick shield. A later experiment of this type at Berkeley [York (52)] led to a reduction in the upper limit to $2 \cdot 10^{-13}$ sec. Two other values for an upper limit on the π° lifetime were derived from cosmic ray experiments. The first cosmic ray value was obtained from an analysis of the R-star [Bradt *et al.* (9)] in

which a shower of some 56 singly charged relativistic particles were observed in a photographic plate exposed in the stratosphere. A considerable multiplication of the number of charged particles in the core of the shower was found and, assuming that this multiplication was due to electron pair production resulting from the decay γ-rays of π°-mesons created in the initial interaction, led to an upper limit on the π° lifetime of $3 \cdot 10^{-13}$ sec. More recently, Lord *et al.* (53) observed an event similar to the R-star except that it was produced by a primary proton (instead of an α-particle) with an energy of the order of 10^{13} e.v. From the observation of a single electron pair about 500μ from the point of collision, they deduce an upper limit on the π° lifetime of $2 \cdot 10^{-15}$ sec. However, this value is subject to considerable doubt since it is based on one electron pair of rather low energy. It therefore appears that the best upper limit on the π° lifetime known at present is $5 \cdot 10^{-14}$ sec.

From a theoretical point of view, the rapid decay of the π°-meson into γ-rays is not at all surprising. As a matter of fact, if we assume that the nucleons obey the Dirac equation and can exist in negative energy states, the π-meson should, by virtue of its coupling to the nucleon field, create a virtual proton-antiproton pair. The proton pair being charged is coupled to the electromagnetic field and the two components of the pair annihilate each other producing at least two final photons [this possibility was first pointed out by Sakata & Tanikawa (54)]. A careful theoretical study [cf. Yang (13)] indicates that the most probable mode of decay of spin-0 π°-mesons is into two photons while spin-1 π°-mesons cannot decay into less than three γ-rays (or an electron-positron pair). Hence, it may be concluded immediately from the observed two-photon decay that the π°-meson possesses spin 0 (or a spin greater than one.) This conclusion is based on general angular momentum and parity arguments and is not subject to the uncertainties of meson field theory. This is not true for the theoretical predictions of the π° lifetime. The weak coupling calculations which have been performed are not only questionable because of the perturbation methods used but actually lead to infinite results and recourse must be had to subtraction techniques [e.g., the method of Pauli regulators—cf. Steinberger (55)] in order to obtain finite answers. Perhaps the only safe statement to make at this time is to say that a lifetime less than $5 \cdot 10^{-14}$ sec. is consistent with the observed two-photon decay of the π°-meson but would be hard to reconcile with three-photon decay or electron pair decay.

Statistics, spins, and parities of the π-mesons.—The two-photon decay of the π°-meson immediately fixes its boson character. The statistics of the charged π-meson can be deduced from a study of the stars resulting from the absorption of slow π^--mesons by nuclei. The large excitation energies associated with π^- disintegrations [cf. Cheston & Goldfarb (56)] indicate that the π^--meson is a boson rather than a fermion. The absorption of slow π^--mesons by heavy nuclei will be discussed more fully in the next section. In this section we shall discuss briefly the experiments on the absorption of slow π^--mesons in hydrogen and deuterium as they bear on the problems of the

statistics, spins and parities of the charged and neutral π-mesons [a more detailed discussion of the hydrogen and deuterium absorption experiments will be found in a review article by the author (57)].

We have already reproduced in Figure 12 the γ-ray spectrum which is observed to accompany the absorption of slow π^--mesons in hydrogen. It was pointed out that accurate determinations of the masses of the charged and neutral π-mesons are made possible by a knowledge of this γ-ray spectrum. For our present purposes, it is to be noted that the occurrence of a discrete γ-ray at the high energy end permits the definite conclusion to be drawn that the charged π-meson is a boson. As far as the spins and parities of the charged and neutral π-meson fields are concerned, the relevant piece of experimental information is the relative probability of mesic to radiative absorption (i.e., the relative probability of the reaction $\pi^-+P\rightarrow N+\pi^\circ$ to $\pi^-+P\rightarrow N+\gamma$) which was found to be 0.94 ± 0.20. By inquiring into the angular momenta and parities of the π°-meson and photon which are emitted, it can be shown that the relative probability of mesic to radiative absorption depends on the spins and parities which characterize the charged and neutral π-meson fields. This type of analysis leads to the conclusion [see Marshak (57)] that the approximate equality between the mesic and radiative absorption probabilities argues for the same parity if both charged and neutral mesons possess spin zero and for opposite parity if the charged meson possesses spin 1 and the neutral meson possesses spin 0.

While the slow π^- absorption experiment in hydrogen provides evidence against certain combinations of the spins and parities of the π-mesons, the corresponding experiment in deuterium is even more clear-cut in its implications. In deuterium, the requirements of energy and momentum conservation do not require the absorption of π^--mesons to be accompanied by the emission of γ-rays or π°-mesons. It is now possible for the rest energy of the π°-meson to be completely converted into the kinetic energies (about 70 M.e.v. apiece) of the two final neutrons in accordance with the reaction scheme: $\pi^-+D\rightarrow N+N$ (we shall term this process neutron absorption). Since the electromagnetic reaction is inherently weak and the 5 M.e.v. mass difference between the π^-- and π°-mesons barely allows the mesic absorption to take place (the $\pi^--\pi^\circ$ mass difference must be larger than the sum of the deuteron binding energy and the neutron-proton mass difference, namely 3.5 M.e.v.), neutron absorption would be expected to be the dominant reaction. However, when the Pauli exclusion principle for the two final neutrons is combined with parity and angular momentum considerations, this conclusion is strongly modified for some of the possible π^--meson fields. For some fields, the reaction: $\pi^-+D\rightarrow N+N+\gamma$ (radiative absorption—involving the emission of two slow neutrons and a high energy γ-ray) acquires a transition probability comparable to or even greater than that for neutron absorption and there is even the possibility of competition from the reaction: $\pi^-+D\rightarrow N+N+\pi^\circ$ (mesic absorption—involving the emission of two slow neutrons and a π°-meson).

Thus, if the π^--meson possesses spin zero and even parity (scalar) no neutron absorption should take place and most π^--mesons should undergo radiative absorption. If the π^--meson possesses spin 0 and odd parity (pseudoscalar), neutron and radiative absorption should compete on roughly comparable terms. If the π^-- and π°-mesons are both scalar or both pseudoscalar, mesic absorption should be negligible whereas if one is scalar and the other is pseudoscalar, about 10 per cent of the π^--mesons should give rise to π°-mesons. If the π^--meson possesses spin 1 and odd parity (vector),

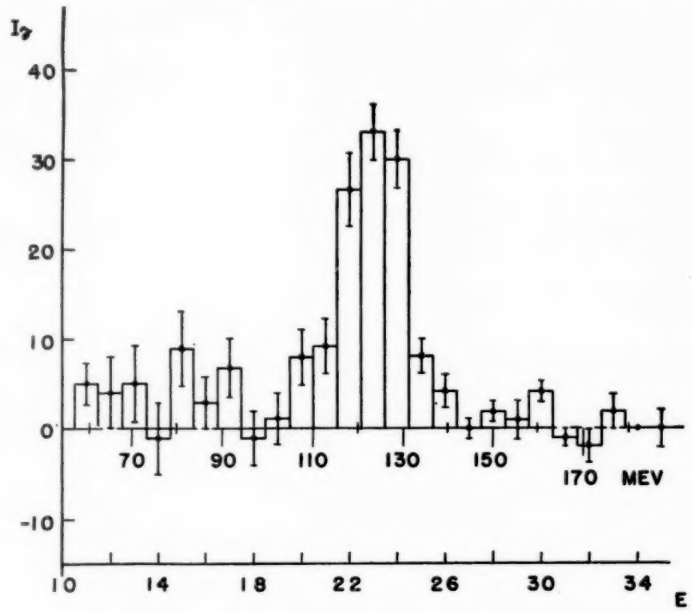

FIG. 13. γ-Ray spectrum from $\pi-$ on deuterium.

neutron absorption should be much more probable than radiative absorption whereas if the π^--meson possesses spin 0 and even parity (pseudovector), the ratio of neutron to radiative absorption should be 2 to 1. Some competition from π° emission (of the order of 10 per cent) should result regardless of the parity of π°.

In view of the strikingly different qualitative theoretical predictions, the experimental results of the π^- absorption in deuterium become of great interest. Panofsky *et al.* (36), using the same apparatus as for the hydrogen absorption experiment, have observed the γ-ray spectrum shown in Figure 13. The conspicuous features of this spectrum are the peak in the neighborhood of 130 M.e.v. (corresponding to radiative absorption) and the absence of γ-rays in the middle energy region (corresponding to mesic absorption). No direct measurement of the neutron absorption probability was made but in-

stead was inferred from the γ-ray experiment by comparing the intensity of the high energy peak with the similar peak in the hydrogen absorption experiment. In addition, a direct comparison of the middle energy γ-rays was made by sending the slow π-mesons first into the high pressure hydrogen gas and then into the high pressure deuterium gas. The respective numbers of counts thus measured are listed in Table VII.

TABLE VII

Type of Absorption	H (counts per minute)	D (counts per minute)
Mesic	0.45 ± 0.09 c/m	-0.007 ± 0.020 c/m
Radiative	0.470 ± 0.046 c/m	0.275 ± 0.034 c/m
Neutron	———	0.65 ± 0.11 c/m

Table VII shows that neutron absorption is just about twice as probable as radiative absorption and that there is no evidence for mesic absorption. These observations enable one to conclude immediately that the scalar and vector fields are excluded for the charged π-meson. Both the pseudoscalar and pseudovector fields for the charged π-mesons are, in view of the theoretical and experimental uncertainties, consistent with the data. If the π^--meson is pseudoscalar, the absence of γ-rays in the middle energy region is some evidence against mesic absorption and for a pseudoscalar π°-meson, although this evidence is not absolutely conclusive because of the experimental error. If the π^--meson is pseudovector, nothing can be said about the π° field on the basis of the deuterium absorption experiment although it will be recalled that the hydrogen absorption experiment favors the pseudoscalar field for π°.

We have seen that a great deal has been learned about the spins and parities of the π-mesons from experiments on the absorption of slow π-mesons in hydrogen and deuterium but we are still not sure about the spin of the charged π-meson and are in some doubt about the parity of the neutral π-meson. We could, of course, invoke the principle of simplicity and argue that the charged and neutral π-mesons should possess the same spin and parity. This would uniquely determine the fields of both charged and neutral π-mesons as pseudoscalar. However, it is essential to establish such a conclusion on direct experimental grounds. One method for determining the spin of the charged π-meson was suggested by Wentzel (58). Wentzel pointed out that if a charged π-meson possesses spin 1, it will have three possible states of polarization and if the π-meson production takes place just above threshold, strongly polarized beams of mesons can be produced—the type of polarization depending on the character of the meson-nucleon coupling. When such a polarized beam of π-mesons undergoes decay into μ-mesons, an anisotropy in the angular distribution of the π-μ decays should result. Several experimenters have looked for a possible anisotropy in the angular dis-

tribution of the $\pi^+ - \mu^+$ decays. In the first photonic production experiment, McMillan *et al.* (1) examined the angular distribution of $\pi^+ - \mu^+$ decays and, and, within statistical error, found an isotropic distribution with respect to the incident photon direction. Powell (34) examined the angular distribution of $\pi^+ - \mu^+$ decays with respect to the downward flux of cosmic ray nucleons and also found a negative result. These results are not conclusive evidence against a spin-1-charged π-meson—apart from their poor statistical accuracy —because of the possibility that large depolarizing effects are at work [cf. Wentzel (58)]. Peterson (59) has found a small positive effect but the anisotropy in the angular distribution of $\pi^+ - \mu^+$ decays which he finds is very peculiar and contrary to all theoretical expectations. One may summarize the present status of the polarization experiment by saying that the evidence is quite inconclusive either way.

A much more promising method [Cheston (60) and Marshak (57)] for determining the spin of the charged π-meson is to measure the cross section for the process: $P+P \rightarrow \pi^+ + D$ and its inverse $\pi^+ + D \rightarrow P+P$. If we denote the cross section for the first process by $\sigma_{1\rightarrow 2}$ and for the inverse $\sigma_{2\rightarrow 1}$, the two cross sections are related by the principle of detailed balancing as follows:

$$\sigma_{2\rightarrow 1} = \frac{2}{3(2S+1)} \frac{p^2}{k^2} \sigma_{1\rightarrow 2}$$

where S is the spin of the π^+-meson, p is the momentum of either proton and k is the momentum of the π^+-meson or the deuteron in the center of mass system. Thus if both $\sigma_{1\rightarrow 2}$ and $\sigma_{2\rightarrow 1}$ are measured, S will be determined. We have already discussed the cross section for the reaction: $P+P \rightarrow \pi^+ + D$ (see above); preliminary measurements made by Clark *et al.* (61) of the cross section for the inverse reaction: $\pi^+ + D \rightarrow P+P$, using the externally focused π^+ beam from the Rochester cyclotron, definitely indicates a spin 0 for the π^+-meson.

Absorption of Slow π^-- and μ^--Mesons by Nuclei

Absorption of slow π^--mesons.—In the previous section, we presented the experimental results on the absorption of slow π^--mesons by protons and deuterons. It was seen that when protons absorbed π^--mesons, high energy γ-rays and π°-mesons are emitted with about equal probability. The deuteron absorption was found to lead to high energy γ-rays in about one-third of the cases; the remaining two-thirds of the π^--mesons absorbed in deuterium led to two high energy neutrons. The large amount of radiative absorption in deuterium, which is surprising at first, became comprehensible when it was explained in terms of the absence of high nucleon momenta in the deuteron. Because (*a*) the binding is greater in nuclei, (*b*) the electromagnetic interaction is inherently much weaker than the nucleon interaction, and (*c*) the emission of π°-mesons is in most cases energetically forbidden and in those cases where it is energetically allowed the statistical factor is smaller

than for nucleon emission, one would expect that the absorption of slow π^--mesons by heavier nuclei would lead chiefly to the emission of nucleons. This expectation is borne out by experiment. Panofsky *et al.* (36) have looked for high energy γ-rays when π^--mesons are stopped in hydrogenous compounds containing lithium and carbon and have found a negative effect. This enables them to place an upper limit of 1 per cent on the radiative and mesic absorption of slow π-mesons in Li and C.

The other type of experiment which has been performed by many authors is to stop π^--mesons in photographic emulsions and to investigate the disin-

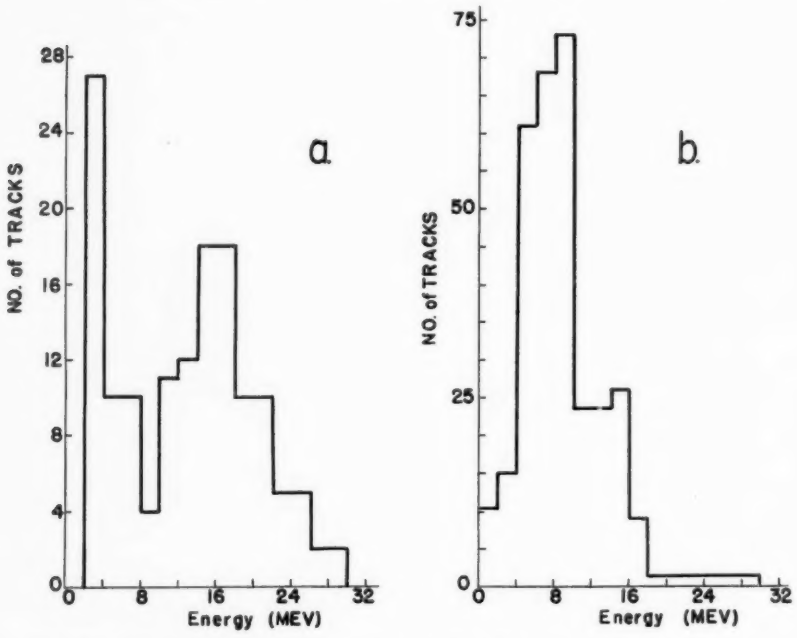

FIG. 14. Energy spectra of alphas (curve *a*) and protons (curve *b*) from π^- disintegrations in photographic emulsions.

tegration products. It is found that about 70 per cent of the π^--mesons which end in the emulsion give rise to nuclear stars with visible prongs. About 30 per cent end without giving rise to any visible prongs (except for occasional small blobs which are assumed to be due to recoil nuclei) which, in view of results of Panofsky *et al.* (36), must be interpreted chiefly in terms of the emission of one or more neutrons unaccompanied by charged particles.

Many workers have used the photographic technique to study π^- disintegrations and we report here the essential experimental results and their qualitative theoretical interpretation. The numbers of π^--meson disintegrations which have been studied are: Perkins (62), 100; Adelman & Jones (63),

500; Cheston & Goldfarb (56), 400; Menon *et al.* (64), 2,500; and Adelman (65), 1,500. Since the last two workers used the same convention for a star prong, namely any group of grains (except an electron track) leaving the terminus of a π^--meson with a well-defined direction, their data are combined to give the frequency-prong distribution of Table VIII. The percentages

TABLE VIII

No. of prongs	0	1	2	3	4	5	6
Percentage of stars	28±2	23.2±0.7	23.2±0.7	16.1±0.6	7.6±0.5	1.4±0.2	0.1±0.1

which are listed should be fairly reliable since they are based on more than 4,000 stars. The energy spectrum of protons less than 30 M.e.v. from one- and two-prong stars is given in Figure 14 [cf. Menon *et al.* (64)] as is the

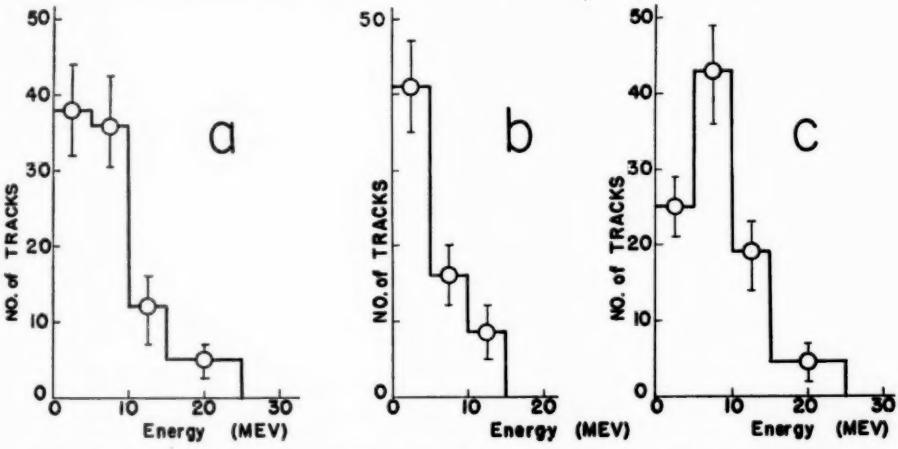

FIG. 15. Energy spectra of alphas from C^{12} (curve *a*), N^{14} (curve *b*) and O^{16} (curve *c*).

energy spectrum of α-particles less than 30 M.e.v. from one-prong stars. The peak of the proton spectrum is at 9.6 M.e.v. and it can be shown that the spectrum fits quite well to a theoretical distribution corresponding to excitation energy about 110 M.e.v. based on the Weisskopf evaporation model. The α-particle spectrum is seen to possess a double peak with the transition point at about 9 M.e.v.; it is very likely that most of the α-particles below 9 M.e.v. come from the light nuclei in the emulsion (CNO) and those above 9 M.e.v. from the heavy nuclei (Ag and Br) because of the difference in the Coulomb potential barriers. If this separation is taken seriously, it is possible to deduce the α/p ratio for light and heavy nuclei and it is found that α/p is equal to $1.0 \pm .1$ for light nuclei and 0.3 ± 0.04 for heavy nuclei. Menon *et al.* (64) have also studied π^--stars produced directly in the gelatine (sandwiched in between layers of emulsion) and have identified the particular light nucleus

of the CNO group responsible for the star from a study of the reaction products. In this way, they have measured the α-particle spectra from the nuclei C, N, and O shown in Figure 15. These α-particle spectra are of interest since they exhibit the effect of the structure of the particular nucleus on the cut-off energy; for the α-particle nuclei C^{12} and O^{16}, the α-particle spectrum extends to about 25 M.e.v. whereas for the α-particle plus deuteron nucleus, N^{14}, the cut-off is at about 15 M.e.v.

In addition to protons less than 30 M.e.v. (chiefly evaporation protons), there is an appreciable number of high energy protons, greater than 30 M.e.v. which can not be explained as the high energy tail of the evaporation spectrum. Cheston & Goldfarb (56), Menon *et al.* (64), and Adelman (65) find that the fraction of π^- absorptions leading to fast protons is 10 ± 2 per cent, 9.5 ± 1.4 per cent, and 9.5 ± 3.3 per cent, respectively. It is worth remarking that some of the stars with high energy protons exhibit visible excitation energies of the order of 100 M.e.v. Such high excitation energies provided the first strong evidence for the boson character of the π^--meson, reference to which has already been made. The fact that only about three-fourths of the available energy appears to be transformed into evaporation nucleons and the presence of a sizeable number of high energy protons can be understood in terms of a π^- absorption mechanism which regards the π^- rest energy of 140 M.e.v. as initially shared among a small number of nucleons which subsequently undergo secondary collisions with other nucleons and thereby heat up the nucleus [Cf. Tamor (66)]. Because of the initial prejudice for neutrons in the elementary act of absorption of the π^--meson by a proton, the knock-on model also predicts a larger fraction of high energy neutrons than high energy protons and proportionately more for the light than for the heavy nuclei. This probably explains most of the 28 per cent of the starless π^- disintegrations seen in the emulsion and the even larger fraction of starless disintegrations observed in the gelatine by Menon *et al.* (64). Most of these starless cases very likely consist of one and occasionally two fast neutrons and a small number of evaporation neutrons. The fact that perhaps 50 per cent of these starless π^- disintegrations have associated blobs, which are presumably due to recoils caused by the emission of high energy neutrons, is further support for this viewpoint. Not all low energy nucleons (less than 30 M.e.v.) need be evaporation products; an appreciable faction may be knock-on nucleons present on the surface of the nucleus and recoiling from collisions with the high energy nucleons. As a matter of fact, Adelman (65) has found some support for this viewpoint in that he has observed a measurable preference for low energy protons in the backward hemisphere with respect to the fast protons.

Thus far, we have only discussed the experimental evidence bearing on the nuclear absorption of π^--mesons by elements no heavier than silver. In the very heavy elements it is to be expected that nuclear fission will seriously compete with ordinary star production. This follows from the fact that the absorption of a π^--meson converts a nuclear proton into a high energy neu-

tron (70 to 90 M.e.v.) which has a sizeable cross section for the fission of uranium and thorium. Thus, the measured fission cross sections for 90 M.e.v. neutrons are uranium: $\sigma = 1.4 \cdot 10^{-24}$ cm.^{2}, thorium: $\sigma = 1.0 \cdot 10^{-24}$ cm.^{2} and bismuth: $\sigma = 0.03 \cdot 10^{-23}$ cm.^{2}. In the case of uranium and thorium, this fission cross section is approximately geometrical whereas for bismuth it is much smaller. Hence, the high energy neutron of 70 to 90 M.e.v. resulting from the absorption of the π^--meson should lead to fission in uranium and thorium but not in bismuth. Bradner (67) has observed about a dozen uranium fissions induced by π^--mesons in uranium specks imbedded in the photographic emulsion. He finds that the lengths of the tracks of the fission fragments are approximately the same as the lengths of tracks of fission fragments produced by high energy neutron bombardment of uranium which in turn do not differ appreciably from low energy neutron bombardment. These observations are in agreement with Serber's hypothesis (68) that high energy nuclear fission first leads to the emission of a sizeable number of low energy neutrons and then proceeds like low energy fission.

Scattering of π-mesons by nuclei.—The slow π-meson interactions with nuclei necessarily involve only the negative variety and take place from the K-shell of the appropriate mesic atom. On the contrary, the fast meson interactions which we now consider involve π-mesons of both signs of charge and take place directly from the continuum. Up to the middle of 1950, data bearing on the nuclear interaction of π-mesons came from cosmic ray experiments performed by Brown & McKay (69), Butler *et al.* (70), and Camerini *et al.* (21), to cite only three contributions. In the latter half of 1950, experiments on the nuclear interaction of π-mesons were performed for the first time with artificially produced π-mesons in the energy region 30 to 100 M.e.v [Bradner & Rankin (71), Bernardini *et al.* (72)].

All the cosmic ray experimenters worked with the particles produced in local penetrating showers in order to avoid confusion with μ-mesons. Two types of apparatus were used: cloud chambers with plates of lead or carbon and photographic emulsions. The cloud chamber experiments suffer from the defect that a shower particle cannot be followed and observed continuously because of the lead plates which, however, are needed in order to distinguish between soft component and penetrating particles. Shower particles which give rise to stars and which are absorbed completely within the lead plates thus escape observation and must be corrected for. Furthermore, there is an additional ambiguity resulting from the fact that it is not possible in general to decide whether the penetrating particle is a π-meson or a proton. Consequently, the geometrical nuclear interaction cross section which is measured does not necessarily refer to π-mesons. Even assuming that the π-mesons constitute most of the penetrating particles in the penetrating shower, it is difficult to decide what fraction of the secondary interactions are absorption events and what fraction scattering events. This is due to the fact that many absorption events may actually be scattering events: thus, a π-meson in suffering a scattering collision may impart sufficient energy to one of the

nucleons in the nucleus to give rise to a star or a charged π-meson may undergo charge exchange scattering (i.e., be converted into a neutral meson in the scattering collision) to be counted as an absorption rather than as a scattering. Most of these difficulties are overcome in the photographic type of experiment where the shower particles are identified as π-mesons by grain density and multiple scattering measurements. In this manner, Camerini *et al.* (21) have studied the nuclear interaction of 29 π-mesons in the energy region 85 to 1300 M.e.v. and the cross section was found to be close to geometrical. Of the 29 stars, 7 were accompanied by single shower particles (in one case the shower particle was identified as a π-meson), whereas 22 were not accompanied by any shower particles. It is likely that the 7 1_p stars are examples of ordinary π-meson scattering and some fraction of the 22 O_p stars are examples of charge exchange scattering (with the π° decaying into two unobserved γ-rays). However, the statistics are still poor and a separation into absorption, direct scattering, and charge exchange scattering cross sections is not really possible.

The experiments with artificially produced π^--mesons were performed by Bradner & Rankin (71) in the energy region 30 to 40 M.e.v. and by Bernardini *et al.* (72) in the energy region 70 to 90 M.e.v. While the statistics are still poor, it is evident that both groups of workers obtain an interaction cross section close to geometrical. Bradner & Rankin (71) surveyed about 10 meters of track length and found about 25 scatterings greater than 30° (of which close to half are scatterings greater than 90°), about 10 one- and two-prong stars and about 5 stoppings (no visible prongs emerging). Bernardini *et al.* (72) in a survey of about 12 meters of track length found a dozen scatterings greater than 90° (5 elastic and 7 inelastic), about 20 stars and about 5 stoppings. One interesting aspect of this work is the observation that the inelastic meson scatterings involve large degradations of energy; on the average about three-fourths of the initial meson energy is lost. This fact, subject to further confirmation, may find its explanation in a rapid decrease of scattering cross section with energy or the suppression of small energy transfers by the Fermi gas of nucleons in the nucleus or a combination of both.

Properties of μ-Mesons

One of the most surprising developments in the field of meson physics during the past few years, accentuated during 1950, has been the dethroning of the μ-meson—the meson most commonly observed in cosmic rays—from its former position of supreme interest for an understanding of nuclear forces and cosmic ray phenomena to its present subsidiary position with hardly any apparent reason for existing at all. Despite the fact that the μ-meson appears to have very little relevance for nuclear forces and nuclear processes in general, we shall discuss the properties of the μ-meson because of the illuminating contrast between it and the π-meson and because it will certainly have to be fitted into any future theory of elementary particles. We shall

discuss the mass, electron decay, spin, statistics, and nuclear interaction of the μ-meson. It should be stated at once that no evidence for the existence of a neutral μ-meson has been obtained; presumably this would be difficult to come by because a μ^0-meson would possess many of the properties of a neutrino. Our discussion will therefore be confined to the charged μ-meson.

Mass.—The value of the mass of the μ-meson is certainly no clue to the tremendous disparity between it and the π-meson. The best value of the μ^+-meson mass follows from the mass ratio of the π^+- to the μ^+-meson, namely 1.31 ± 0.02, determined in the Berkeley cyclotron by magnetic curvature and range [Barkas (73)], and the value of 277.6 ± 1.1 electron masses for the mass of the charged π-meson obtained in the same way [Barkas *et al.* (35)]. One finds in this way a μ^+ mass equal to 212 ± 4 electron masses. The μ^- mass almost certainly possesses the same mass as the μ^+-meson and evidence for this equality is given by a recent experiment by Lederman *et al.* (74) in which $\pi^- - \mu^-$ decays were observed in a cloud chamber in a magnetic field. These authors found a value 209 ± 4 electron masses for the μ^- mass.

Electron decay.—A great many cosmic ray experiments have been performed to determine the lifetime for electron decay of the μ-meson. The best cosmic ray determination was made by means of a method of delayed coincidences by Rossi & Nereson (75) in 1942, who obtained the value $2.15 \pm 0.07 \cdot 10^{-6}$ sec. In 1950, Alvarez (76) measured the lifetime of the μ^+-meson using artificially produced π^+-mesons as the source of the μ^+-mesons; the μ^+ decay was detected with scintillation counters operating in delayed coincidence and a value of $2.09 \pm .03$ μ sec. was derived from a curve covering an intensity variation of 10^4. This is probably the most accurate value for the μ^+ lifetime. Within experimental error, the μ^- lifetime is the same as the μ^+ [Lederman *et al.* (74)].

The true nature of the decay particles resulting from the spontaneous disintegration of the μ-meson has only recently been elucidated. For a long time, it was thought that the μ-meson decays into an electron and neutrino with about 50 M.e.v. apiece. However, in 1947, Anderson *et al.* (77) obtained the first definite example of a decay electron with an energy of about 25 M.e.v. Soon thereafter many experimentalists began to find evidence for the nonuniqueness of the electron energy, and it is now certain that the μ-meson emits a continuous spectrum of electrons. Several measurements of this electron spectrum were carried out during 1950, but the most accurate electron spectrum which has been measured up to the present time is still the one obtained by Leighton *et al.* (78) in 1949. These authors found the energy spectrum shown in Figure 16; it is seen that the spectrum extends from 9 to 55 M.e.v. with a mean energy of about 34 M.e.v. The observed average energy of 34 M.e.v. for the electron argues against more than two neutral particles in addition to the electron since an average energy of 34 M.e.v. is just about one third of the μ-meson rest mass energy. This best spectrum is still not good enough to justify detailed comparison with theory.

We have referred to the charged particle resulting from the decay of the μ-meson as an electron; this statement must be proved. The best demonstration that the charged decay particle possesses an electronic mass comes from an experiment by Hincks & Pontecorvo (79) performed in 1950, who investigated the penetration of the charged decay particles through various absorbers. The *Bremsstrahlung* intensities which they measured leads to the conclusion that the charged particle must possess a mass less than two electronic masses. Further support for the electronic nature of the charged particle decay from the μ meson comes from the observation of the collision of a decay particle with an electron in a photographic emulsion where the energies before and after the collision were measured by the scattering method [Cam-

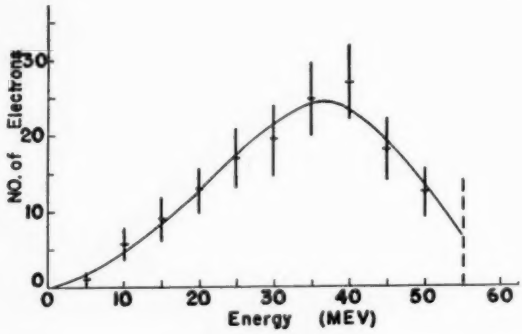

FIG. 16. Electron energy spectrum from decay of μ-meson.

erini & Fowler (80)]. It is therefore very likely that the charged decay particle is indeed an electron.

It is still necessary to fix the nature of the neutral particles resulting from the decay of a μ-meson. It was believed for a long time, the evidence coming from an analysis of the soft component, that not all of the μ-meson energy is converted into electrons and γ-rays. Hincks & Pontecorvo (81) and Sard & Althaus (82), however, performed direct experiments, looking for coincidences between the decay electrons and materialized γ-rays to ascertain whether any of the neutral decay particles are photons; their result was completely negative. These experimental results lead to the following unique decay scheme for the μ meson (if we restrict ourselves to known neutral particles of vanishing rest mass): $\mu^+ \rightarrow e^+ + 2\nu$ where ν represents a neutrino. This decay scheme would imply immediately that the μ-meson is a fermion. The above decay scheme is also consistent with the decay scheme $\pi \rightarrow \mu + \nu$ for the π-μ decay. The work of Christy & Kusaka (83) on the burst production by μ-mesons makes it very likely that if the μ-meson is a fermion, it possesses spin 1/2. These authors show that the frequency of large bursts of ionization produced by very energetic μ-mesons is too low to be reconciled with spin 1 for the μ-meson but could be reconciled with spin 0 or spin 1/2. Presumably,

μ-mesons possessing spin 3/2 or higher would also lead to a much greater frequency of burst production by μ-mesons in the cosmic radiation than is observed.

The great differences in the rates and products of nuclear absorption of slow μ^-- and π^--mesons underlines, as does no other set of experimental facts, the striking differences between the two types of mesons both as regards their intrinsic properties and their interaction with nucleons. In contrast to the π^--meson which undergoes absorption by all nuclei including hydrogen, once the K-shell of the appropriate mesic atom is reached, the μ^--meson only undergoes nuclear absorption for Z greater than or equal to about 10. As Z decreases below 10, nuclear absorption loses out very rapidly to the electron decay process. In other words, when Z is equal to 10, the lifetime for the nuclear absorption of the μ^--meson is equal to the lifetime for electron decay, that is to say, $2.1 \cdot 10^{-6}$ sec. The corresponding lifetime for nuclear absorption of the π^--meson for $Z = 10$ is of the order of 10^{-20} sec., a factor of about 10^{14}. Since the μ-meson is a decay product of the π-meson, it is possible to regard the absorption of a μ^--meson by a proton in a nucleus as a two-step process [a possibility first pointed out by Marshak & Bethe (49)], in accordance with the scheme:

$$\mu^- + P \begin{cases} \nearrow \pi^- + \nu + P \\ \searrow \mu^- + \pi^+ + N \end{cases} N + \nu.$$

In other words, the μ^--meson may virtually create a π^--neutrino pair or the proton a π^+-neutron pair, both of which possibilities lead to the same final state of neutron plus neutrino. The probability for this indirect coupling of the μ^--meson to the proton can be calculated from a knowledge of the strength of the coupling of the charged π-meson to the nucleon and the lifetime for π-μ decay: the result is in reasonable agreement with experiment. The indirect coupling scheme evidently predicts that the absorption of a μ^--meson by a nucleus will be accompanied by the emission of a neutrino. The prediction that the nuclear absorption of a μ^--meson will be accompanied by the emission of a light neutral particle like the neutrino has the consequence that the residual nucleus would be expected to be left in a state of low excitation energy, of about 15 M.e.v. on the average [cf. Rosenbluth (84) and Tiomno & Wheeler (85)]. An excitation energy of the order of 15 M.e.v. would explain the qualitatively different phenomena which are associated with nuclear absorption of μ^-- and π^--mesons despite the fact that the masses of the μ^-- and π^--mesons differ only by 30 per cent. Whereas 72 per cent of the π^- absorptions produce nuclear stars with visible prongs, it was only quite recently that George & Evans (86) have shown that 7.5 ± 1.5 per cent of the μ^- absorptions give rise to visible prongs (about 90 per cent are one-prong stars and the remainder are two-prong stars). George & Evans (86) were able to demonstrate this fact by exposing photographic emulsions deep underground and taking advantage of the fact that at 20 to 60 meters water equiv-

alent underground, the π^--mesons are absorbed out and most of the nuclear stars must be due to μ^--mesons. This experiment is consistent with an average excitation energy of the order of 15 M.e.v. as are the experiments by Sard *et al.* (87) [cf. Groetzinger & McClure (88)] who detected neutrons resulting from the nuclear absorption of μ^- mesons in lead. By slowing down the neutrons and using appropriate slow neutron counters, Sard *et al.* (87) were able to show that an average neutron multiplicity of 1.9 ± 0.2 is associated with the nuclear absorption of μ^--mesons, which is again consistent with an average excitation energy of the order of 15 M.e.v. The question still remains whether the light neutral particle which accompanies the nuclear absorption of a μ^--meson and departs with most of the available energy may be a γ-ray. Piccioni (89), some time ago, looking for high energy γ-rays resulting from μ^--mesons stopping in iron, was able to show that there are no γ-rays above 20 M.e.v. The evidence is therefore very strong that the absorption of a μ^--meson leads to the emission of a neutrino.

The extremely slow rate of nuclear absorption of μ^--mesons proves that the μ-meson-neutrino field is very weakly coupled to the nucleon field. This deduction is consistent with the fact that no evidence has been obtained from accelerator experiments for the direct single production of μ-mesons. Suppose, however, that a strong interaction exists between the μ-meson-pair field and the nucleon field. This would be reconcilable with the decay of μ^--mesons from the K-shells of light elements since energy conservation would prohibit any nuclear reaction from proceeding through the μ-meson-pair field. However, a strong coupling between the μ-meson-pair field and the nucleon field would require direct production of μ-meson pairs when sufficient energy is available (this has thus far not been disproved), a sizeable cross section for nuclear scattering of fast μ-mesons and rapid absorption of the penetrating component of the cosmic rays below sea level. The experimental evidence against the latter two consequences appears to eliminate the possibility of a strong coupling between the μ-meson-pair field and the nucleons.

What is this experimental evidence? Some of the early experiments on μ-meson scattering, e.g., by Code (90) and Shutt (91) led to an upper limit on the cross section of $5 \cdot 10^{-28}$ cm^2 per nucleon. During 1950, Amaldi & Fidecaro (92) carried out the most elaborate μ-meson scattering experiment yet conducted with a counter-hodoscope setup and determined that the scattering cross section was less than $5 \cdot 10^{-30}$ cm.^{2}/nucleon for meson energies greater than 300 M.e.v. and less than $1 \cdot 10^{-28}$ cm.^{2}/nucleon for energies between 180 and 300 M.e.v. The fact that the upper limit on the nuclear scattering cross section is several orders of magnitude smaller than geometrical implies that coupling of the μ-meson-pair field to nucleons is weak and much smaller than any reasonable theory would predict [cf. Wentzel (93)]. Therefore, it is likely that the only coupling of the μ meson to the nucleon is through the μ-meson–neutrino field and we have already shown that this coupling is 10^{14} times weaker than the π-meson coupling. Corresponding to

such a weak coupling, the nuclear scattering of μ-mesons would be completely unobservable.

The second group of experiments which indicates a weak coupling of μ-mesons to nuclei is the deep penetration of cosmic rays underground. Cosmic rays have been detected at a depth of 3,000 meters water equivalent [Nishina (94)] and there is every reason to believe that they penetrate much deeper still. These penetrating particles cannot be π-mesons or protons or electrons and the most plausible explanation is that they are μ-mesons. Furthermore, the observed variation of cosmic ray intensity with underground depth can be explained in terms of electromagnetic interactions (chiefly ionization processes) and π-μ decay [cf. Greisen (95) and Hayakawa & Tomonaga (96)]; it is not necessary to invoke any sizeable nuclear interaction for the μ-mesons. However, a cross section much smaller than geometrical for nuclear interaction of energetic μ-mesons is not excluded by the underground experiments and actually George & Evans (97) have been able to detect a cross section of 10^{-29} cm^2/nucleon for star production by μ-mesons. By exposing photographic emulsions at depths up to 60 meters water equivalent and showing that there is a slow variation of the frequency of star production with depth parallel to the variation in the μ-meson intensity, they obtained the above cross section. A cross section of this order of magnitude is explicable in terms of the virtual photon field associated with the highly energetic charged μ-mesons and the empirical value of the photon cross section for the production of stars, of the order of 10^{-28} cm^2/nucleon [cf. Miller (98) and Kikuchi (99)]. Applying the Weiszsacker-Williams method to the present problem, it can easily be shown that a μ-meson of energy E is equivalent to a beam of photons of frequency distribution ω given by

$$N(\omega)d\omega = \frac{2}{\pi}\frac{e^2}{\hbar c}\log\left(\frac{E}{\hbar\omega}\right)\frac{d\omega}{\omega}.$$

Therefore, the cross section for star production if

$$\sigma = \int_{E_t}^{E} \sigma_p(\omega)N(\omega)d\omega$$

where σ_p is the experimental cross section for photo-star production at energy $h\omega$ and E_t is the threshold energy for star production. Recent experiments by Miller (98) and Kikuchi (99) indicate a star production cross section at 300 M.e.v. of about the same magnitude as the meson production cross section, namely 10^{-28} cm.^{2}/nucleon. Substituting numbers into the above formula leads to a cross section of 10^{-29} cm.^{2}/nucleon for star production by μ-mesons possessing an energy of the order 10^{10} e.v.

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RECENT DEVELOPMENTS IN THE THEORY OF NUCLEAR STRUCTURE[1]

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Introduction

A major problem of contemporary nuclear physics is the determination of the quantum numbers of nuclear states. These quantities include parity, total angular momentum (I), energy (E) and, for excited states, the various partial level widths (Γ_n); there are also several of a more or less approximate character including the intrinsic spin (S), the orbital angular momentum (L), the charge multiplet (T), and the supermultiplet ($PP'P''$ or the equivalent partition symbol). Information on quantum numbers has been derived from measurements of spins, magnetic and quadrupole moments, selection rules for electromagnetic transitions and beta decay, simple theoretical formulas for half-lives of excited states, correlations between properties of successive transitions, and the dependence of reaction cross sections on energy and angle (1).[2] Simple models based on quasi-molecular and quasi-atomic approximations (2 to 7) have also proved useful in fixing quantum numbers, particularly when used to supplement incomplete experimental information.[3]

[1] This review is essentially a survey of papers published in 1950.

[2] The monograph by Devons (1) contains an excellent survey of experimental methods and results and theoretical ideas relating to nuclear structure through 1948.

[3] A review of all recent publications on nuclear structure is impossible within the limits of this essay. Among the important problems and developments not discussed may be mentioned:

(a) the quantitative evaluation of mass relations in the region of heavy nuclei; (b) systematic evaluation of nuclear radii and α decay constants employing new data on artificial α-emitters; (c) improved packing fraction measurements; (d) improved mass determinations for light nuclei; (e) measurements of γ, n thresholds and analysis of γ radiation from slow neutron capture; (f) correlations between the magic numbers and asymmetric fission, the absence of stable isotopes of certain elements, the occurrence of odd-odd nuclei in nature, and the cross sections for fast neutron capture; (g) the influence of nuclear charge and current distribution and polarizabilities on the hyperfine structure of atomic levels and on the elastic scattering of energetic electrons, positrons, and γ radiation; (h) the phenomenological theory of exchange currents and moments; (i) the doublet splitting in He^5 and Li^5; (j) the nature of the first excited state of Li^7; (k) experimental and theoretical studies on 2, 3, and 4 particle problems; (l) critical studies of the j-j coupling scheme in light nuclei; (m) theory of photoelectric disintegrations in light nuclei; (n) critical evaluation of the assignments of single particle quantum numbers to excited states appearing in radioactive and isomeric transitions; (o) applications of the Thomas-Fermi statistical method to the study of shell structure; (p) evidence for simple relations in the spacing of energy levels;

Evidence for Charge and Supermultiplets

The equality of the specifically nuclear forces between neutrons and between protons has been inferred from (*a*) the existence of a long series of stable nuclei containing equal numbers of neutrons and protons and (*b*) the semiquantitative accord between the calculated Coulomb energy differences and decay energies in the series of mirror nuclei ($N=Z'=Z+1$, $N'=Z=Z'-1$). The short half lives of the radioactive decay processes in the series of mirror nuclei are consistent with the view that the ground state wave functions of the parent and daughter systems are nearly identical as required by the assumed approximate invariance of the nuclear Hamiltonian under the substitution $N'=Z$ and $Z'=N$. The stronger statement that the two states belong to the same supermultiplet (in this case a single charge multiplet with $S=1/2$ and $T=1/2$) is a reasonable inference from the occurrence of well-defined allowed favored and unfavored groups in the distribution of comparative half lives. For ground states the validity of the supermultiplet analysis means that the space wave functions possess the maximum possible symmetry consistent with the exclusion principle.

A further consequence of the assumed invariance property is that mirror nuclei should have similar level schemes. The resemblance in level spacing should be particularly close for low lying levels in highly stable systems. Large distortions are to be expected near the limit of the discrete spectrum and beyond because of the relatively large differential effect of the Coulomb interaction on lightly bound systems.

The level schemes of C^{13} and N^{13} show little resemblance. Levels at 2.37 and 3.52 M.e.v. in N^{13} may possibly be correlated with those at 3.10 and 3.91 M.e.v. in C^{13}. Thomas (8) and Ehrman (9) find a semiquantitative explanation for the different excitation energies of these nuclei in the small binding energy of the odd proton in N^{13}. In fact the energy required to remove a proton from N^{13} is only 1.84 M.e.v. while the removal of a neutron from C^{13} requires the comparatively large energy 4.87 M.e.v.

It has been observed that the Be^7-Li^7 Coulomb energy difference falls below the smooth empirical curve determined by the other $4n+3$ mirror systems. A related discrepancy occurs in the location of low excited states. In Li^7 the excitation energy is 0.478 M.e.v.; in Be^7 the recently discovered excited state occurs at 0.429 M.e.v.[4] These differences can be correlated in a consistent manner with the small binding energy of Be^7 relative to He^4 and He^3 components (10). The same calculation requires the radius of Be^7 to exceed that of Li^7 by approximately 10 per cent.

Early experimental studies of proton-proton and neutron-proton scatter-

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(*q*) evidence for nonuniform particle density from asymmetric fission and the lengths of fission decay chains; (*r*) the possibility that the ground states of N^{14} and P^{32} have odd parity as suggested by the long half lives of C^{14} and P^{32}.

[4] The magnetic spin-orbit coupling of the *p* shell nucleons may account for an appreciable fraction of the difference in excitation energies [Inglis (74)].

ing led to the conclusion that singlet S interactions are almost identical for like and unlike two-particle systems.[5] This conclusion provides the basis for a far reaching generalization contained in the statement that the specifically nuclear forces are independent of the charge state (proton or neutron) of the interacting particles. Recent experimental results on the scattering of high energy protons and neutrons are apparently incompatible with charge independence (11), although some difference of opinion exists on this point (12, 13). Nevertheless the identification and classification of nuclear states from the point of view of charge independence is likely to develop into an indispensable source of information regarding the properties (including deviations from charge independence) of the nuclear forces (14).[6]

Magnetic Moments and L-S Coupling for Odd Mass Number

The magnetic moments for odd A (15, 16) are plotted in Figure 1 (odd Z) and Figure 2 (odd N). The theoretical interpretation of these diagrams is based on the study of simple limiting situations. Results of great value have been derived from the assumption that the nucleus possesses a definite orbital angular momentum L and a total angular momentum $I=L+1/2$ or $I=L-1/2$ (doublet states and L-S coupling). The magnetic moment is given by the formula

$$\mu = g_L(I-\tfrac{1}{2}) + \tfrac{1}{2}\cdot g_s, \qquad I = L+\tfrac{1}{2} \qquad 1.$$

$$= \frac{I}{I+1}\left[g_L(I+\tfrac{3}{2}) - \tfrac{1}{2}\cdot g_s\right], \qquad I = L-\tfrac{1}{2} \qquad 2.$$

Here

$$\begin{aligned} g_s &= 5.58 \text{ (odd proton)} \\ &= -3.82 \text{ (odd neutron)} \end{aligned} \qquad 3.$$

while g_L depends on special properties of the model. The following two extreme models have been employed in this connection (7).

Extreme single particle model.—The odd nucleon moves in a spherically symmetric field of a core containing all the other particles. Even parity and zero angular momentum are assigned to the core in harmony with the empirical rule that even-even nuclei have always zero spin in the ground state. All angular momentum and parity properties are associated with the odd nucleon. Thus

$$\begin{aligned} g_L &= 1 \text{ (odd proton)} \\ &= 0 \text{ (odd neutron).} \end{aligned} \qquad 4.$$

The dashed curves in Figures 1 and 2 are the Schmidt limits computed from equations 1 to 4. It is not difficult to see that the experimental points group

[5] A small discrepancy first revealed by the careful analysis of G. Breit and his collaborators has been traced to the charge dependence of magnetic interactions between two nucleons (75).

[6] The extensive experimental material on charge multiplets and on the location of singlet levels in B^{10} and N^{14} is reviewed by Lauritsen in this volume (76). The writer is indebted to Richards (77) and Ajzenberg (78) for information on the same topics.

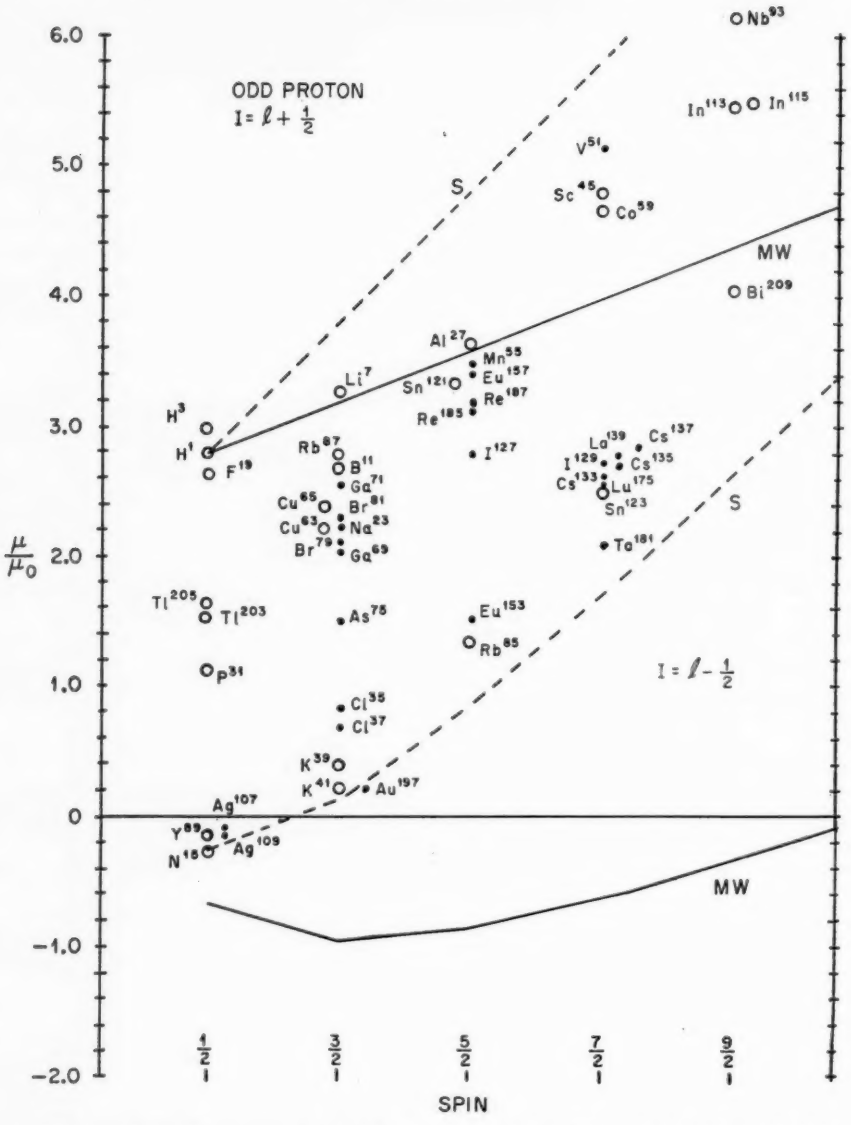

FIG. 1. Magnetic moments for odd values of Z. Dashed lines are the Schmidt one particle limits, solid lines the Margenau-Wigner uniform model limits. Circles denote nuclei with one particle missing from a closed shell or one particle in excess of the number to make up a closed shell.

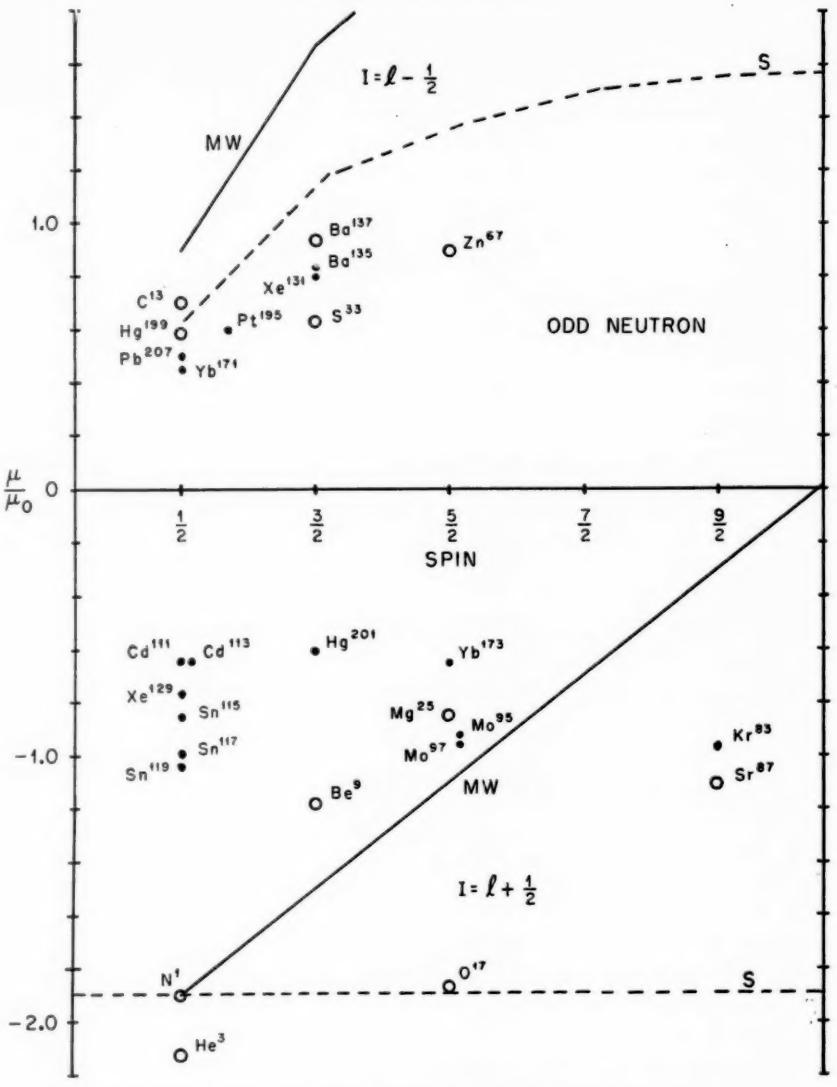

FIG. 2. Magnetic moments for odd values of N. Dashed lines are the Schmidt one particle limits, solid lines the Margenau-Wigner uniform model limits. Circles denote nuclei with one particle missing from a closed shell or one particle in excess of the number to make up a closed shell.

themselves into two broad bands between the theoretical limits and paralleling them. Relative to the Schmidt limits there is no apparent distinction between closed (± 1) shell systems[7] and others not of that type.

The fact that all experimental moments lie close to or between the Schmidt limits supports the assumption of a predominantly doublet character for the low states of odd mass nuclei. It must be considered unlikely that a widespread occurrence of strong quartet components would never result in a breach of the limits.

Uniform model.—This model distributes the orbital angular momentum uniformly over all the particles in the nucleus with the result

$$g_L \sim Z/A \sim 0.4 \qquad 5.$$

for both odd N and odd Z. The solid lines in Figures 1 and 2 are the Margenau-Wigner limits computed from equations 1, 2, 3, and 5. Moments falling between the MW limits are interpreted as evidence that the orbital angular momentum is not a constant of motion. States with $L=I-1/2$ and $L=I+1/2$ may have the same parity in a many particle system and, consequently, may combine to produce intermediate values of the moments.

From the point of view of quasi-atomic approximations, L-S coupling and the extreme single particle picture are most likely to attain a noticeable degree of validity for closed (± 1) shell systems. The evidence is summarized in the following tabulation listing closed (± 1) shell nuclei[8] and ground state configurations:

(*a*) Supporting L-S coupling

H_1^3, He_2^3—$(1s_{1/2})^{-1}$

F_9^{19}—$(2s_{1/2})^{-1}$

(*b*) Supporting L—S coupling and the extreme single particle picture

C_6^{13}, N_7^{15}—$(1p_{-1/2})^{-1}$

O_8^{17}—$(1d_{5/2})^1$

$K_{19}^{39,41}$—$(1d_{3/2})^{-1}$

Rb_{37}^{85}—$(1f_{5/2})^{-1}$

Y_{39}^{89}—$(2p_{1/2})^1$

Ba_{56}^{137}—$(nd_{3/2})^{-1}$

Pb_{82}^{207}—$(np_{1/2})^{-1}$

(*c*) Consistent with L-S coupling and the uniform model

Li_3^7—$(1p)^2(1p)^1$ or $(1p_{3/2})^1$

Be_4^9, B_5^{11}—$(1p_{3/2})^{-1}$ or $(1p)^3(1p)^{2n}$

Mg_{12}^{25}, Al_{13}^{27}—$(1d_{5/2})^{-1}$ or $(1d)^5(1d)^{2n}$

In Li^7 the three particles in p orbits may be considered as equivalent

[7] One particle lacking to complete a shell or one particle in excess of the number required for a closed shell.

[8] Closed shells at N or $Z=6$, 14, 28 and 38 are predicted by the spin-orbit model. Other closed shells are common to both the central elevation and spin-orbit schemes.

yielding $g_L \sim 1/3$; the He^4-H^3 model yields a better value, $g_L \sim 3/7$. The two complementary systems with N and $Z=13$ are represented by an O^{16} core and extra-core nucleons in $1d$ orbits. The spin-orbit model generates a closed subshell at N or $Z=14$ by placing six like particles in $d_{5/2}$ orbits; N or $Z=13$ then represents an almost closed shell. One value of g_L is satisfactory for both $N=13$ and $Z=13$. Similar remarks apply to the complementary pair Be_4^9 and B_5^{11} with N or $Z=5$ (three like particles in $1p$ orbits, one short of a closed $p_{3/2}$ subshell). The location of these points relative to the MW limits suggests 90 per cent $P_{3/2}$ and 10 per cent $D_{3/2}$.

(*d*) Intermediate between the S and MW limits for $I=L+1/2$; fairly close approach to L-S coupling.

Sc_{21}^{45}—$(1f_{7/2})^1$
Co_{27}^{59}—$(1f_{7/2})^{-1}$ or $(1f)^7$
Sr_{38}^{87}—$(1g_{9/2})^{-1}$
$In_{49}^{113,115}$—$(1g_{9/2})^{-1}$
Nb_{41}^{93}—$(1g_{9/2})^1$

Eight intermediate and heavy nuclei have moments falling outside of the MW limits. It is noteworth that six of these (listed above) contain closed (± 1) shells. Thus the exceptional cases from the point of view of the uniform model occur most frequently where failures are not unexpected.

(*e*) Failure of L-S coupling

P_{15}^{31}—$(2s_{1/2})^1$
$Cu_{29}^{63,65}$—$(2p_{3/2})^1$
$Tl_{81}^{203,205}$—$(ns_{1/2})^1$
Bi_{83}^{209}—$(1h_{9/2})^1$

If all closed (± 1) shell points now are removed from the magnetic moment diagrams, the remaining points fall between the Schmidt limits for $I=L-1/2$ and the MW limits for $I=L+1/2$. No explanation of this peculiar fact has yet been advanced.

The complete absence of points between the Schmidt and MW limits for $I=L-1/2$ also calls for explanation. Reasonable variations in g_L from one system to another would be expected occasionally to place experimental points between these limits if L-S coupling held to a high degree of approximation. One may infer that a general failure of L-S coupling masks the expected reasonable variation in g_L.

An improved description of nuclear states can be realized by combining features of the single particle and uniform models. The ground state is represented as a linear combination of doublet components, one, generally large, approximating the single particle picture with $L=I\pm 1/2$ and the other, generally small, approximating the uniform picture with $L=I\mp 1/2$, both components having the same parity:

$$\Psi = \alpha\Psi_{L=I\pm 1/2} + (1-\alpha^2)^{1/2}\Psi_{L=I\mp 1/2}.$$

The coefficient α can be computed by an interpolation procedure using the

measured magnetic moment and the appropriate S and MW limits. Results for odd N and odd Z agree closely on the range odd N or $Z<53$ [Davidson (16a); cf. Shawlow & Townes (17a)].

Many pairs of isotopes have the same ground state spin and nearly equal magnetic moments. Gordy (17) has pointed out that the quadrupole moments are also simply related. With two significant exceptions, these regularities conform to the rule that, when there is no change in spin, the increase in the even member of the N,Z pair by two shifts the magnetic moment toward the nearer Schmidt limit (18) and reduces the magnitude of the quadrupole moment (19). This rule suggests that the increase in the even member of the N, Z pair by two with no change in spin tends to reduce deviations from the extreme single particle model or from L-S coupling or both. For odd Z, there may be a connection with the fact that the binding energy of the odd proton increases as neutron pairs are added. The exceptions noted above are $Eu_{63}^{151,153}$ and $Cs_{55}^{133,135,137}$.

The one example where two protons are added with no change in spin is Cd_{48}^{113}, Sn_{50}^{115}. In this case, the moments are almost midway between the limits, and the ambiguity is resolved in favor of the rule by an appeal to shell theory which assigns even parity to these nuclei.

When N is odd the addition of two neutrons without change in spin also tends to shift the magnetic moment toward the nearer Schmidt limit. Examples are $Cd_{48}^{111,113}$, $Sn_{50}^{115,117,119}$, $Te_{52}^{123,125}$, and $Ba_{56}^{135,137}$.

The ratio of hyperfine structure splittings in Rb^{85} and Rb^{87} does not agree with the value calculated from the ratio of the moments, the former quantity being larger by 0.33 ± 0.05 per cent. Bohr & Weisskopf (20) develop an explanation based on the assumptions of volume distributions of intrinsic spin and orbital moments and a common value of g_L; arbitrary linear combinations of $L=I\pm1/2$ are implicitly admitted (79). Numerical results for $g_L=1$ and $g_L=0.43$ are interpreted as evidence for the validity of the single particle as opposed to the uniform model. Actually, the assumption of a common value of g_L seems arbitrary in the application to two isotopes with different spins; $g_L(Rb^{85})=1$ and $g_L(Rb^{87})=0.4$ are reasonable inferences from Figure 1 and yield almost perfect agreement with the experimental excess of 0.33 per cent. In the application to $K^{39,41}$, excellent agreement is obtained with $g_L=1$ for both isotopes (21).

Foldy & Milford (22) propose a "tidal" force mechanism to account for deviations from the Schmidt limits. The nonspherical wave function of the odd nucleon is coupled through the nuclear forces to surface waves of the core, resulting in a sharing of orbital angular momentum between the odd nucleon and the core. The results are promising, although not completely in accord with experiment. Other closely related models are discussed in the next section.

Several authors (23) have suggested that the anomalous component of the proton and neutron magnetic moments is greatly reduced in complex nuclei. One may argue that the effect should appear most clearly in closed (±1) shell systems where the approximation to the extreme single particle

picture is closest. On this view, a substantial modification of the nucleon moments in complex systems is difficult to reconcile with the magnetic moments of N^{15}, O^{17}, F^{19}, K^{41}, Y^{89}, and Pb^{207}, all quite close to the appropriate Schmidt limits and all of the closed (± 1) shell type.

Quadrupole Moments of Odd Mass Nuclei

Several authors have pointed out indications of a relation between shell structure and electric quadrupole moments of odd mass nuclei (17, 24, 25). Gordy gives plots of Q against Z and $|Q|$ against N. Townes, Foley & Low find that the known moments suggest a single curve when Q is plotted against the odd member of the N, Z pair. The single curve is indeed quite plausible if neutron and proton particle densities are strongly correlated so that a distortion of one from spherical symmetry requires a similar distortion of the other. A related effect has been observed in the calculation of non-uniform particle densities where the outward displacement of the protons because of Coulomb repulsion requires a similar displacement of neutrons.

Small negative quadrupole moments at Cu_{29}^{69}, Ge_{32}^{73}, Sb_{51}^{121}, Sb_{51}^{123}, and Bi_{83}^{209} and positive moments at B^{511}, Al_{13}^{27}, S_{16}^{35} and $In_{49}^{113,115}$ are in qualitative agreement with expectations for closed (± 1) shells. However, the quadrupole moments of $In_{49}^{113,115}$ and Sb_{51}^{123} are too large to be produced by a single proton, and the extremely large quadrupole moments in the region centered about $Z \sim 72$ exceed the possibilities of the extreme single particle model by orders of magnitude.

A spheroidal core offers possibilities for large quadrupole moments. Coupling between the total angular momentum of the whole nucleus and the symmetry axis of the core is required to maintain a nonspherical charge distribution with respect to external fields. Rainwater (26) shows that the model of an odd particle moving in a spheroidal potential well generated by a spheroidal core has the required coupling and a minimum energy associated with a definite departure from the spherical shape. The energy of the spheroidal system contains a quadratic term in the eccentricity from the change in surface and Coulomb energies of the core and a linear term from the shift in the eigenvalue of the extra-core particle.

Minimum energy and maximum flattening along the axis of quantization occur for $|m_l| = l (l > 2)$.[9] Spherical symmetry for closed shells results from the vanishing of the mean energy displacement when summed over all values of m_l.

This model seems capable of giving even larger Q values than are observed for closed ($+1$) shell systems. However, if the core has a component of orbital angular momentum $|m_l| = l$ along its axis, it will precess about the total angular momentum vector with a considerable reduction in the effec-

[9] Minimum energy and maximum elongation along the axis of quantization take place at $m_l = 0$ for $l = 1$. The lowest level for $l = 2$ is degenerate, $|m_l| = 2$ and $m_l = 0$ yielding the same displacement, the former with positive and the latter with negative eccentricity. What this means for the quadrupole moment has not been discussed.

tive or time average departure from the spherical shape (19). A second correction results from the finite depth of the potential well (27).

When several nucleons are placed in extra-core orbits, the distortion from the spherical shape depends on the statistical weights of the various m_l states in the extra-core wave function. A strong representation of small m_l values is required to account for the large positive quadrupole moments observed for partly filled shells. This statement provides a criterion for testing the validity of proposed coupling schemes if the approximation of a single configuration is considered adequate for calculating quadrupole moments.

Considerations related to those of Rainwater, but from a more general standpoint, are advanced by Bohr (19). The asymmetry of the core is not explained but is taken as the starting point for a discussion of various possible types of coupling between the angular momentum vectors associated with the odd nucleon and the rotational motion of the core (the latter treated as a symmetrical top).

The anomalous positive quadrupole moment found for Li^7 by Kusch is discussed in two recent theoretical papers. Avery & Blanchard (28) construct wave functions within the $(1p)^3$ ground state configuration consistent with experimental information on the magnetic and quadrupole moments of Li^7 and the K-capture decay properties of Be^7. Satisfactory agreement is found with a ground state wave function predominantly of the [21] symmetry type. This may be compared with Wigner's first approximation [in (1); (14)] in which the low levels of Li^7 and Be^7 are assigned to a [3] supermultiplet. Since a complete breakdown of the supermultiplet classification is unlikely, the result of Avery & Blanchard provides support for the contention that good nuclear wave functions cannot be constructed within a single configuration.

The calculation of Present (29) proceeds from assumptions at the opposite extreme from those of Avery & Blanchard (28). A number of excited configurations in addition to $(1p)^3$ are used to construct completely symmetrical wave functions (symmetry type [3]). The principal result is that a positive quadrupole moment is possible with a pure $^2P_{3/2}$ state of symmetry type [3] and odd parity if configuration interaction is large. The inclusion of a small $^2D_{3/2}$ component of symmetry type [3] and odd parity permits a fairly large positive quadrupole moment with a moderate amount of configuration interaction. The influence of configuration interaction of the magnetic moment and K-capture properties are also studied.

The Classification of Isomeric Transitions

Revolutionary developments occurred in this subject while the present review was being written. The interested reader should consult the original paper of Goldhaber & Sunyar (29a).

The Interpretation of Comparative Half-Lives and Spectral Shapes in the Theory of β-Decay

Recent publications (30, 31, 32) meet the urgent need for accurate charts of the allowed f function and for a tabulation of energies, half lives, branch-

ing ratios, and ft values of all transitions for which the experimental studies are sufficiently accurate and complete (as of June, 1950) to permit the calculation of the ft product.

Theoretical studies of the image transitions yield information on the connection between comparative half lives (ft values) and the ground state quantum numbers, the proportions of Fermi and Gamow-Teller type components in the β-decay theory, and possible deviations from L-S coupling.

The general β-decay theory based on a linear combination of the five covariant coupling schemes yields a linear combination of Fermi and Gamow-Teller type nuclear matrix elements for allowed transitions[10]

$$|M|^2 = \sum_{m_f} \left[G_F \left| \left(f \left| \sum_{k=1}^{A} \tau_{\zeta k} \right| i \right) \right|^2 + G_{GT} \left| \left(f \left| \sum_{k=1}^{G} \tau_{\zeta k} \vec{\sigma}_k \right| i \right) \right|^2 \right] \qquad 6.$$

in which i is the initial and f the final state, the m_f summation is over all values of the final state magnetic quatum number, and τ_k, σ_k are the usual charge and spin operators of the nucleons. Since the half life varies inversely as $|M|^2$ the product $|M|^2 ft$ should be nearly constant in the range of allowed transitions if G_F/G_{GT} is chosen properly. Complete explicit formulas for $|M|^2$ are known under the special assumptions of L-S coupling and the identity of the ground state space wave functions of parent and daughter nuclei (33). The latter assumption should hold generally for image transitions and, to a fair degree of approximation, also for $He^6 \rightarrow Li^6$, and $F^{18} \rightarrow O^{18}$.

The antisymmetric coupling scheme of Critchfield (34) and Wigner requires $G_F = G_{GT}$; this relation has been tested by Moszkowski (32a). The presence of the Fermi type component does appear to improve the constancy of the $|M|^2 ft$ product; however, the indicated value of G_F/G_{GT} is considerably smaller than 1.

In view of the importance of the image transition problem, a more general formulation is desired. Dropping the restriction to pure L-S coupling, the ground state solutions may contain components with $L = I + 1/2$ (statistical weight $\sin^2\theta$) and $L = I - 1/2$ (statistical weight $\cos^2\theta$). The general formula for $|M|^2$ is then (35)

$$|M|^2 = \tfrac{1}{4} G_F + \frac{G_{GT}}{4I(I+1)} [(I+1)\cos^2\theta - I\sin^2\theta]^2. \qquad 7.$$

Destructive interference appears in the GT matrix element and is particularly effective for states in which the $L = I + 1/2$ component predominates. While this study is still in progress, the need for the Fermi component in the general linear combination of the five covariant coupling schemes is emphasized by the possibility of deviations from L-S coupling.

Allowed unfavored transitions are characterized by the selection rules $\Delta I = 0, \pm 1$ (no) and change in supermultiplet (33). In simpler terms, the transition is favored if the same space wave function occurs in both daughter

[10] This formula holds only if the real scalar, polar vector, tensor, and axial vector coupling constants (C_S, C_V, C_T, C_A) satisfy the Fierz relations (45)

$$C_S C_V = C_T C_A = 0.$$

and parent nuclei, while it may be allowed, but with a reduced value of the nuclear matrix element, if there is a substantial difference in the space wave functions (change in symmetry or configuration or both). The actual occurrence of unfavored transitions shows that the supermultiplet classification is only approximate, and mixing of symmetry types does occur. The comparative half lives are in the range 10^4 to 10^6. Shell model considerations (6) are particularly helpful in distinguishing between allowed and first forbidden transition when $ft \sim 10^6$.

An admixture of components belonging to higher supermultiplets in the ground state wave functions with statistical weights ranging from 1 to 5 per cent is required by the observed ratio of ft values in favored and unfavored transitions between ground states of odd mass nuclei. The absence of an obvious trend with mass number in the unfavored ft values has been noticed by several writers (6, 36, 37).

Experimental information on 1st forbidden transitions with $\Delta I = \pm 2$ is accumulating rapidly (38, 43). At least fifteen examples have been established with reasonable certainty on the basis of spectral shape and comparative half life as well as conformity to the requirements of shell models. The importance of these transitions for nuclear structure derives from the fact that they fix the relative parity of orbitals in different shells and greatly reduce uncertainty in the assignment of angular momentum. With respect to the theory of β-decay, they demonstrate the need for tensor or axial vector coupling between the nucleon and lepton fields. These coupling types are also required by the G-T selection rules for allowed transitions.

The characteristic energy distribution associated with $\Delta I = \pm 2$ (yes) differs from the allowed distribution by the factor (39, 40)

$$a = 1/12[W^2 - 1 + \lambda(Z, W)(W - W_0)^2]. \qquad 8.$$

In many applications, $\lambda(Z, W)$ may be replaced by $\lambda(0, W) = 1$ without appreciable error, but accurate numerical values of λ are required when Z is large, particularly in conjunction with $W - 1 \ll 1$.

The appropriate f function for these transitions is $f_1 = \langle a \rangle f$ in which f is the allowed function and $\langle a \rangle$ is an average over the allowed energy distribution. To a useful degree of approximation

$$f_1 \sim 1/20(W_0^2 - 1)f. \qquad 9.$$

Equation 9 can be derived by using $(W-1)(W_0-W)$ as a simple representation of the allowed energy distribution. The same approximation has been used to compute approximate formulas for $f_2[\Delta I = \pm 3$ (no)] and $f_3[\Delta I = \pm 4$ (yes)] [see (43)]. It is found that $(W_0^2-1)ft$ is more nearly constant than ft for transitions with the unique first forbidden shape factor a[(38, 43, 44)]; also, the criterion $(W_0^2-1)ft \sim 10^{10}$ has proved useful in directing attention to likely examples of this first forbidden type (i.e., Cl^{38}) (44).

Feenberg & Trigg (30) plot histograms showing the distribution of log ft values. The transitions identified as $\Delta I = \pm 2$ (yes) are excluded since the ft value (with f the allowed function) is not a suitable criterion for distinguishing this type of transition. Separate plots are provided for (a) odd A, transi-

tions between ground states; (*b*) all transitions for odd A, all transitions involving an excited state of the even-even nucleus for even A; (*c*) even A, all transitions between ground states.

This classification is motivated by the empirical rule that even-even nuclei have zero spin in the ground state. Thus under (*c*) one of the two states involved in a transition has zero spin and presumably even parity. There is little distinction between the observed distributions under (*a*) and (*b*); perhaps the outstanding difference is the large number of allowed unfavored transitions under (*b*) in the range $\log ft \sim 4$ to 5.

Under (*a*) and (*b*) a well defined peak centered at $\log ft \sim 6.2$ is interpreted as predominantly first forbidden [$\Delta I = \pm 1$, 0 (yes)] since all possibilities for allowed transitions are exhausted by the favored and unfavored classifications. For even A the outstanding feature of the empirical ft distribution is the complete absence of a group in the range $\log ft \sim 5.7$ to 6.7 corresponding to the well defined first forbidden group for odd A centered at $\log ft \sim 6.2$.

The interpretation of the missing group depends on the matrix element or elements which are dominant in the odd A transitions. In this connection, the discussion by Feenberg & Trigg (30) is not sufficiently general and is also in error in associating the $\vec{\alpha}$ matrix element with tensor coupling theory.

De Groot & Tolhoek (45) have investigated allowed transitions in the general theory involving all covariant coupling types. These authors postulate that transition probabilities for positron and negatron emission have the same form when effects produced by the Coulomb field of the nucleus are neglected. From the postulate and the assumption of real coupling constants, they obtain the result that the permissible linear combinations are scalar-axial vector-pseudoscalar or polar vector-tensor.

Selection rules and comparative half lives for allowed unfavored and forbidden transitions under the condition of pure L-S coupling are of interest in connection with examples where the half life falls outside of the classification derived from the spin change (46, 47).

Configuration Analysis and the Rule $L=l$, $I=j=l\pm\frac{1}{2}$

The spins of odd mass nuclei are generally in agreement[11] with the angular momenta assigned to the odd particle by current shell model considerations. In these models, the ground state wave function is derived from a configuration containing an odd number of equivalent single particle orbitals. The analysis of the configurations into invariant subspaces with respect to the group of rotations and permutations yields generally several linearly independent doublet states for nearly all values of L in a range beginning at $L=0$ or $L=1$ and extending beyond $L=l$. Table I shows the possible doublet states for partially filled shells containing an odd number of particles in equivalent orbits (7). An important feature of the table is the maximum or near maximum degeneracy at $L=l$. For p, d, and f orbitals (with one exception) maximum degeneracy occurs first at $L=l$. For g or-

[11] $Mn_{25}^{55}(I=5/2)$ and Ho_{67}^{165}, Lu_{71}^{175}, $Ta_{73}^{181}(I=7/2)$ are exceptions.

TABLE I

NUMBER OF LINEARLY INDEPENDENT DOUBLET STATES IN x^n, n ODD*

Configuration \ L	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
$p^{1,5}$		1																
p^3		1	1															
$d^{1,9}$			1															
$d^{3,7}$		1	2	1	1	1												
d^5	1	1	3	2	2	1	1											
$f^{1,13}$				1														
$f^{3,11}$		1	2	2	2	2	1	1	1									
$f^{5,9}$		4	5	7	6	7	5	5	3	2	1	1						
f^7	2	5	7	10	10	9	9	7	5	4	2	1	1					
$g^{1,17}$					1													
$g^{3,15}$		1	2	2	3	3	2	2	2	1	1	1						
$g^{5,13}$	3	5	10	11	15	14	15	13	13	10	9	6	5	3	2	1	1	
$g^{7,11}$	5	15	24	31	37	39	40	39	36	32	27	22	17	13	9	6	4	2
g^9	8	19	35	40	52	54	56	53	53	44	40	32	26	19	15	9	7	4

* For p, d, and f orbitals taken from Gibbs, Wilber & White (80); for g orbitals taken from unpublished calculations by Hammack (81).

bitals, a well defined plateau begins at $L=l$. There appears to be a close correlation between the ground state spin and the degeneracy of different L values derived from configuration analysis.[12]

TABLE II

NUMBER OF LINEARLY INDEPENDENT SINGLET STATES IN x^n, n EVEN*

Configuration \ L	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
$p^{0,6}$	1																	
$p^{2,4}$	1		1															
$d^{0,10}$	1																	
$d^{2,8}$	1		1		1													
$d^{4,6}$	2		2	1	2		1											
$f^{0,14}$	1																	
$f^{2,12}$	1		1		1		1											
$f^{4,10}$	2		4	1	4	2	3	1	2	1								
$f^{6,8}$	4	1	6	4	8	4	7	3	4	2	2		1					
$g^{0,18}$	1																	
$g^{2,16}$	1		1		1		1		1									
$g^{4,14}$	3		5	2	6	3	6	3	5	2	3	1	2		1			
$g^{6,12}$	7	3	13	11	19	13	21	14	17	12	13	7	9	4	4	2	2	
$g^{8,10}$	10	7	24	20	34	28	37	28	34	24	26	17	18	10	10	5	5	2

* For p, d, and f orbitals taken from Gibbs, Wilber & White (80); for g orbitals taken from unpublished calculations by Hammack (81).

[12] The symmetry arguments of the next section appear adequate to account for the empirical regularities. However, a direct connection between degeneracy and the

The notion of a relatively inert core is common to all shell models. Here a certain ambiguity enters because the division into core nucleons and nucleons inhabiting single particle orbitals is somewhat arbitrary. In the extreme single particle model, all nucleons but one are placed in the core. The more general model based on configuration analysis puts all the nucleons belonging to the even member of the N, Z number pair into a core along with all closed shells of particles belonging to the odd member of the number pair. Other variations are possible; among them are the following: suppose that there are n nucleons of one kind in excess of the number required to complete a closed shell. Consider a series of possible core systems containing A-1, A-3, $\cdots$ A-n particles. Let $Q(1, \cdots A\text{-}1)$, $Q(1, \cdots A\text{-}3)$, $\cdots$ $Q(1, \cdots A\text{-}n)$ represent the accurate ground state wave function of these cores while $U_{m_l m_s}$ denotes the single particle orbitals. Then the product functions

$$\begin{aligned} &Q(2, \cdots A)U_{m_l m_s}(1) \\ &Q(4, \cdots A)U_{m_{l1} m_{s1}}(1) \cdots U_{m_{l3} m_{s3}}(3) \\ &\cdots \\ &Q(n+1, \cdots A)U_{m_{l1} m_{s1}}(1) \cdots U_{m_{ln} m_{sn}}(n) \end{aligned} \qquad 10.$$

and all functions derived from them by permutations of co-ordinates can be used to construct properly antisymmetrized wave functions with definite values of the angular momentum quantum numbers L, S, M_L and M_S.

One problem of interest is the number of linearly independent doublet wave functions with prescribed values of L in the antisymmetrized function space defined by equation 10. Two extreme situations are easy to discuss. In the first, the quasi-atomic approximation is assumed to be quite good for both core and extra-core nucleons. In that event, the function space defined by a particular line of equation 10 includes the spaces defined by all preceding lines. This statement requires only that the core function $Q(P, \cdots A)$ is contained in the function space generated by all possible permutations of co-ordinates acting on all functions of the type

$$Q(P+2, \cdots A)U_{m_{l1} m_{s1}}(P+1)U_{m_{l2} m_{s2}}(P).$$

The first n-1 lines of equation 10 add nothing to the possibilities present in the last line. Consequently the degeneracies are just those listed in Table I.

The second extreme situation is based on the assumption that the quasi-atomic picture is rather poor for both core and extra-core nucleons. Then the function spaces generated by the separate lines of equation 10 overlap relatively little, and the total degeneracies may be estimated by adding the degeneracies computed from each line separately. This procedure gives the results displayed in Table IV. Judging from the relative magnitudes of the degeneracies displayed in Tables I and III, the emphasis on the states with $L=l$ is greatest in the second extreme situation; the correlation with the level scheme of the extreme single particle picture (top line of equation 10) is

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quantum numbers of the ground state may be sought in the dependence of configuration interaction on degeneracy. It is satisfactory that conclusions based on symmetry considerations are not likely to be upset by configuration interaction.

TABLE III

NUMBER OF LINEARLY INDEPENDENT DOUBLET STATES IN $x^n+x^{n-2}+\cdots+x^1$, n ODD

Configuration \ L	0	1	2	3	4	5	6	7	8	9	10	11	12
p^1		1											
$p^3+\cdots$		2	1										
$p^5+\cdots$		3	1										
d^1			1										
$d^3+\cdots$		1	3	1	1	1							
$d^5+\cdots$	1	2	6	3	3	2	1						
$d^7+\cdots$	1	3	8	4	4	3	1						
$d^9+\cdots$	1	3	9	4	4	3	1						
f^1				1									
f^3+		1	2	3	2	2	1	1	1				
$f^5+\cdots$		5	7	10	8	9	6	6	4	2	1	1	
$f^7+\cdots$	2	10	14	20	18	18	15	13	9	6	3	2	1
$f^9+\cdots$	2	14	19	27	24	25	20	18	12	8	4	3	1
$f^{11}+\cdots$	2	15	21	29	26	27	21	19	13	8	4	3	1
$f^{13}+\cdots$	2	15	21	30	26	27	21	19	13	8	4	3	1
g^1					1								
g^3		1	2	2	4	3	2	2	2	1	1	1	
$g^5+\cdots$	3	6	12	13	19	17	17	15	15	11	10	7	5
$g^7+\cdots$	8	21	36	44	56	56	57	54	51	43	37	29	22
$g^9+\cdots$	16	40	71	84	108	110	113	107	104	87	77	61	48
$g^{11}+\cdots$	21	55	95	115	145	149	153	146	140	119	104	83	65
$g^{13}+\cdots$	24	60	105	126	160	163	168	159	153	129	113	89	70
$g^{15}+\cdots$	24	61	107	128	163	166	170	161	155	130	114	90	70
$g^{17}+\cdots$	24	61	107	128	164	166	170	161	155	130	114	90	70

most pronounced when the quasi-atomic approximation is particularly poor.

All the preceding considerations can be applied to even-even nuclei. The results for the degeneracies of singlet states are shown in Tables II and IV. A striking property of the singlet degeneracies is the relatively high degeneracy of ^1S states. This circumstance is helpful in understanding the empirical rule that even-even nuclei have always zero spin in the ground state.

Jahn (49) gives a complete analysis of d^pd^q configurations[13] with respect to the symmetric and rotation groups, generalizing earlier work on the first neutron-proton p shell. A further analysis with respect to the group of unitary transformations in the five dimensional space of the orbital states of a single d particle yields information on the probable order of levels. One interesting detail is the prediction of $^1S_0$ or $^3S_1$ ground state for odd-odd nuclei with $N=Z$, in agreement with the beta-decay of F^{18} and P^{30},[14] but contrary to the measured spin of Na^{22}_{11} ($I=3$). For odd mass number, the predicted ground state is $^2D_{3/2}$ or $^2D_{5/2}$ in agreement with the shell model rule.

[13] That is, p neutrons and q protons in equivalent d orbits.

[14] Thus reducing the weight of evidence for a $2s$ orbital at N or $Z=9$ and 15.

RACAH'S SYMMETRY THEOREM, THE SHELL MODEL RULE $L=l$, $I=j$, AND RELATED TOPICS

The most successful version of the shell model is based on the hypothesis of strong spin-orbit coupling (2 to 5). The empirical relations require a splitting of roughly 1 to 2 M.e.v. between single particle levels with $j=l-\frac{1}{2}$

TABLE IV

NUMBER OF LINEARLY INDEPENDENT SINGLET STATES IN $x^n+x^{n-2}+\cdots+x^0$, n EVEN

Configuration \ L	0	1	2	3	4	5	6	7	8	9	10	11	13
p^0	1												
$p^2+\cdots$	2		1										
$p^4+\cdots$	3		2										
$p^6+\cdots$	4		2										
d^0	1												
$d^2+\cdots$	2		1		1								
$d^4+\cdots$	4		3	1	3		1						
$d^6+\cdots$	6		5	2	5		2						
$d^8+\cdots$	7		6	2	6		2						
$d^{10}+\cdots$	8		6	2	6		2						
f^0	1												
$f^2+\cdots$	2		1		1		1						
$f^4+\cdots$	4		5	1	5	2	4	1	2	1			
$f^6+\cdots$	8	1	11	5	13	6	11	4	6	3	2		1
$f^8+\cdots$	12	2	17	9	21	10	18	7	10	5	4		2
$f^{10}+\cdots$	14	2	21	10	25	12	21	8	12	6	4		2
$f^{12}+\cdots$	15	2	22	10	26	12	22	8	12	6	4		2
$f^{14}+\cdots$	16	2	22	10	26	12	22	8	12	6	4		2
g^0	1												
g^2	2		1		1		1		1				
$g^4+\cdots$	5		6	2	7	3	7	3	6	2	3	1	2
$g^6+\cdots$	12	3	19	13	26	16	28	17	23	14	16	8	11
$g^8+\cdots$	22	10	43	33	60	44	65	45	57	38	42	25	29
$g^{10}+\cdots$	32	17	67	53	94	72	112	73	91	62	68	42	47
$g^{12}+\cdots$	39	20	80	64	113	85	133	87	108	74	81	49	56
$g^{14}+\cdots$	42	20	85	66	119	88	139	90	113	76	84	50	58
$g^{16}+\cdots$	43	20	86	66	120	88	140	90	114	76	84	50	58
$g^{18}+\cdots$	44	20	86	66	120	88	140	90	114	76	84	50	58

and $j=l+\frac{1}{2}$. This magnitude may be compared with the depths of the potential well (about 28 M.e.v.) and the volume component of the binding energy per particle (about 14 M.e.v.). Clearly, the spin-orbit interaction is small relative to effectively spin-independent components in the nuclear Hamiltonian.

The assumptions of complete j-j coupling corresponds to an extreme situation in which the spin-orbit interaction is the dominant term in the Hamiltonian operator. This assumption is not required to account for the successes of the spin-orbit model; nevertheless some emphasis has been placed on it (3) and it is an interesting special case to investigate. Racah has proved a valuable theorem on the symmetry properties of wave func-

tions constructed from products of orbitals all having the same n, l, and j. The theorem is essentially the evaluation of the statistical weight $W(I)$ of the symmetrical coupling between pairs of like particles (50, 51). The early work of Wigner on the symmetry properties of nuclear states demonstrates the usefulness of such considerations in a more general context (14).

A pronounced tendency toward maximum symmetry in the space co-ordinates consistent with the exclusion principle may be inferred from the mass relations of isobars, the grouping of allowed β transitions into well-defined favored and unfavored classes, and the four-group structure observed in light nuclei. It is, therefore, reasonable to postulate that the order of the levels is strongly influenced by the values of $W(I)$, the lowest level having the largest value of $W(I)$. An equivalent statement is that the state with maximum symmetry in the space co-ordinates is expected to lie lowest. Because of the exclusion principle $W(I)$ is identical with the statistical weight of singlet couplings between pairs of like particles. The latter quatity is given by the diagonal matrix elements of the operator:

$$W = \frac{1}{4}\sum_{p<q}(1 - \sigma_p \cdot \sigma_q). \tag{11.}$$

The general formula obtained from equation (11) is

$$W(I) = \frac{1}{8}n(n-1) + \frac{nj(j+1) - I(I+1)}{2(2l+1)^2}. \tag{12.}$$

Maximum $W(I)$ occurs at the minimum possible value of I; thus $I=0$ is favored energetically for even-even nuclei in agreement with the empirical rule that even-even nuclei have $I=0$ in the ground state.

For odd mass number, the minimal I allowed by the exclusion principle coincides with the j of the odd particle only for closed (± 1) shells. Otherwise $I_{\min}$ is $\frac{3}{2}$ for three particles in a shell or three particles lacking to complete a shell and in other cases is $\frac{1}{2}$. Bearing in mind the empirical rule $I=j$, it is a reasonable inference from the above theorem that spin-orbit coupling effects are not large enough to produce a near approach to j-j coupling.

Calculations on odd-odd nuclei support the above inference (50). Extreme j-j coupling is inconsistent with the spin and magnetic moment of Li^6. The criterion of maximum symmetry requires $I=3(p_{3/2}p_{3/2})$ while the state with $I=1$ derived from $p_{3/2}p_{3/2}$ is unsatisfactory with respect to the magnetic moment.

In the space orbital approximation (l and s are not coupled), the eigenvalues of the operator W are

$$W(L, S) = \tfrac{1}{2}n(n+2) - \tfrac{1}{2}S(S+1). \tag{13.}$$

The criterion of maximum $W(L, S)$ requires that the ground state be a singlet ($S=0$) for even n and doublet ($S=\frac{1}{2}$) for odd n in agreement with Wigner's earlier and more general considerations. Since $W(L, S)$ is actually independent of L, a more searching symmetry criterion is required. Racah introduces an operator q_{ik} which has the eigenvalue $2l+1$ when applied to a $^1S_0$ function of the variables i and k and zero otherwise. The diagonal matrix elements of the operator

$$Q = \sum_{i<k} q_{ik} \qquad 14.$$

then depend on L, S and n. It is reasonable to associate the lowest level with the largest diagonal matrix element (or eigenvalue) of Q since the part of an accurate wave function representing pairs of like particles with relative orbital angular momentum different from zero makes no contribution to the potential energy when the range of the forces is small.

The eigenvalues of Q are found to be

$$Q_n(L, S) = \tfrac{1}{4}(n - v)(4l + 4 - n - v) \qquad 15.$$

in which v is the "seniority number" of the L, S state, i.e., the smallest number of equivalent orbitals required to generate a state with the given L, S quantum numbers. Maximum Q occurs for minimum v:

$$\begin{aligned} &{}^1S_0\ (v = 0) \text{ for } n \text{ even} \\ L = l, \qquad &S = \tfrac{1}{2}(v = 1) \text{ for } n \text{ odd.} \end{aligned} \qquad 16.$$

The rule $L=l$ or $I=j$ therefore favors the space orbital over the j-j coupling approximation.

Mayer (3) and Kurath (52) have derived the rule $I=j$ from a simple force model applied to j-j coupling configurations. The Hamiltonian operator includes a strong spin-orbit interaction and a weak short range radial potential between pairs of like nucleons. The latter term causes a splitting in first order of the degenerate zero order level associated with the configuration. Results are $I=j$ (odd n) and $I=0$ (even n) for the ground state levels if the range of the radial interaction terms is sufficiently small compared to nuclear dimensions. As the range is increased, crossing of levels occurs within the configuration and the level order goes over to that defined by Racah's considerations. These calculations are of interest mainly as showing the wide range of conditions under which it is possible to maintain the rule $I=j$ (odd n) and $I=0$ (even n) for the ground state levels. The basic assumption that a close approach to j-j coupling persists in a many particle system or even a two particle system appears to go beyond the experimental evidence.

Spins of Odd-Odd Nuclei and β-Decay Selection Rules

Nordheim (37) has generalized the shell model rule $L=l$, $I=j=l\pm\frac{1}{2}$ to odd-odd nuclei. The two odd groups are assigned spin $L_1=l_1$, $I_1=j_1$ and $L_2=l_2$, $I_2=j_2$ where j_1 and j_2 denote the toal angular momentum of the two odd nucleons as prescribed by the spin-orbit model. Then I_1 and I_2 are compounded to produce the resultant I in accordance with the following rules:

(*a*) If $j_1=l_1\pm\frac{1}{2}$ and $j_2=l_2\mp\frac{1}{2}$, the total spin is $|I_1-I_2|$.

(*b*) If $j_1=l_1\pm\frac{1}{2}$ and $j_2=l_2\pm\frac{1}{2}$, I_1 and I_2 combine to a large resultant spin (presumably greater than the larger of the two). These rules tend to maximize the triplet component in the ground state wave function.

Since no details are given by Nordheim (37), the writer has tested the rules on Feingold's tabulation of experimental information and *ft* values supplemented by the United States National Bureau of Standards circular on nuclear data (53). For the majority of odd-odd isotopes, j_1 and j_2 are not

uniquely fixed by the values of N and Z as is shown by the following incomplete list of closely competing orbitals in different ranges of N and Z:

$$29\text{–}37 \cdots p_{3/2}, f_{5/2}$$
$$39\text{–}49 \cdots p_{1/2}, g_{9/2}$$
$$51\text{–}57 \cdots d_{5/2}, g_{7/2}$$
$$59\text{–}81 \cdots d_{5/2}, d_{3/2}, s_{1/2}, h_{11/2}.$$

When two or more configurations are available, it is not surprising that usually at least one provides a spin value and parity conforming to the requirements of the beta decay data. In many such cases, the rules are sustained, but definite predictions of spin and parity would not have been possible in the absence of the beta decay information.

Table V contains examples for which the transition between ground states is consistent with Nordheim's rules. These are selected by the criteria (*a*) only one configuration is available or (*b*) if more than one configuration is available only one yields spin and parity consistent with the information on the β-decay. Examples which do not fulfill these criteria add little to the evidence supporting the rules. Again the absence (or low intensity) of the

TABLE V

EXAMPLES OF TRANSITIONS BETWEEN GROUND STATES CONSISTENT WITH NORDHEIM'S RULES

Odd-Odd Nucleus	log ft	Configuration	Spin	Parity
B_5^{10}	13.65	$p_{3/2}\ p_{3/2}$	2, 3*	even
B_5^{12}, N_7^{12}	4.18	$p_{1/2}\ p_{3/2}$	1	even
N_7^{14}†	9.05	$p_{1/2}\ p_{1/2}$	1*	even
N_7^{16}	6.84	$s_{1/2}\ p_{1/2}$	0	odd
F_9^{18}	3.57	$s_{1/2}\ s_{1/2}$	1	even
Na_{11}^{22}§	13.8	$d_{3/2}\ d_{3/2}$	2, 3*	even
P_{15}^{30}	4.71	$s_{1/2}\ s_{1/2}$	1	even
Cl_{17}^{36}	13.49	$d_{3/2}\ d_{3/2}$	2*, 3	even
Cl_{17}^{38}‖	7.44	$f_{7/2}\ d_{3/2}$	2	odd
K_{19}^{42}‖	8.02	$f_{7/2}\ d_{3/2}$	2	odd
Ga_{31}^{70}	5.08	$p_{1/2}\ p_{3/2}$	1	even
Y_{59}^{90}‖	7.98	$d_{5/2}\ p_{1/2}$	2	odd
Y_{39}^{92}¶	7.58	$d_{5/2}\ p_{1/2}$	2	odd
Pr_{59}^{142}**	7.93	$h_{9/2}\ d_{5/2}$	2	odd

* Experimental value.

† Still a puzzle because of the long half life of C^{14} [cf. Gerjuoy (82) for a discussion of the possibility that N_7^{14} has odd parity in the ground state].

§ Either the rule $I=j$ fails or the $d_{3/2}$ level lies below $d_{5/2}$ at N or $Z=11$.

‖ $\Delta I=\pm 2$ (yes) confirmed by shape of spectrum and value of log $(W_0^2-1)\,ft$

¶ log $(W_0^2-1)\,ft\sim 9.4$.

** log $(W_0^2-1)\,ft\sim 9.5$.

transition between ground states in Sc_{21}^{46}, Sc_{21}^{48}, V_{23}^{48}, Mn_{25}^{52} and in V_{23}^{52}, Mn_{25}^{56}, Co_{27}^{56}, Co_{27}^{58} is consistent with the rules, the configurations being $f_{7/2}f_{7/2}$ for the first group and $p_{3/2}f_{7/2}$ for the second (only one configuration is available in each example). The transitions from $Li_3^8(p_{3/2}p_{3/2})$, $Al_{13}^{28}(s_{1/2}d_{5/2})$, and $Y_{39}^{88}(g_{9/2}p_{1/2}$ or $p_{1/2}g_{9/2})$ to excited states of the product nuclei are all in accord with the rules.

Two examples where the rules fail are mentioned by Nordheim (37). These are Li^6 with $I=1$ and K^{94} with $I=4$. The rules require $I=2$ or 3 from $p_{3/2}p_{3/2}$ and $I=2$ from $d_{3/2}f_{7/2}$.

A different type of exception where the spin-orbit model does not provide a suitable configuration occurs at $Z=45$, 47, and 49. Here the available orbits are $p_{1/2}$ and $g_{9/2}$ for the odd proton and $d_{5/2}$, $d_{3/2}$, $s_{1/2}$, and $h_{11/2}$ for the odd neutron. There is no way of compounding these orbits to produce a state of even parity with $I=0$ or 1. However the β transitions between ground states from Rh_{45}^{106}, Ag_{47}^{106}, Ag_{47}^{108}, Ag_{47}^{110}, In_{49}^{112}, In_{49}^{114}, In_{49}^{116}, and In_{49}^{118} are all of the allowed unfavored type (log $ft\sim4.3$–5.3) requiring $I=0$ or 1 and even parity for the ground state of the odd-odd nucleus. The possibility of a $g_{7/2}$ orbit in the odd neutron range may be considered momentarily,[15] but is it clear that the arbitrary disruption of a once closed shell, particularly one with a large value of j, is not a desirable expedient.

Electric Dipole Transitions

Pronounced resonance maxima for the capture of energetic γ-radiation have been observed in a number of elements. The total oscillator strength is comparable with the Z of the nucleus. Goldhaber & Teller (54) relate this effect to a collective type of simple harmonic motion in which the protons as a group are displaced relative to the neutrons as a group (55). Jensen (56) presents a critical discussion of the experimental and theoretical relations. Levinger & Bethe (57) propose an alternative explanation based on a many level picture of photon absorption; semiquantitative results for the cross section and mean absorption energy are derived from dipole and quadrupole sum rules. The influence of exchange forces on the dipole sum (58) is an important factor in the calculations. Because of the probable high viscosity of nuclear matter the two points of view may be closely related (54).

Steinwedal & Jensen (59) develop a hydrodynamical formalism for the study of collective motions in a two-phase liquid drop. Formulas for the frequency, line width, and oscillator strength are derived with the aid of two mathematically convenient, but physically arbitrary assumptions. These are (*a*) volume energy density $\sim(\rho_p-\rho_n)^2/(\rho_p+\rho_n)$ and (*b*) $\rho_p+\rho_n=$ constant. The second assumption puts a severe constraint on variations of the neutron and proton particle densities within the nucleus. A related calculation of the dependence of particle density on position (60) verifies the natural expectation that variations from uniformity must be small if the neutron and proton densities are artificially constrained to vary in opposite directions.

[15] This is indeed the interpretation given by Nordheim (private communication).

The statistical theory of the γ, n and γ, p reactions in its original form fails (61) to predict the large cross sections and nonuniform angular distributions observed for energetic particles from medium and heavy elements (62 to 65). Modifications to meet these difficulties have been proposed by Schiff (66). Radical departures from the statistical theory are also under consideration. Courant (67) and Jensen (68) suggest that the normal evaporation type process involving an initial general partition of the energy over many particles must be supplemented by a direct photoelectric process in which nearly all the energy is given to a single particle. Courant (69) finds that the observed strong maximum in the intensity perpendicular to the direction of the incident beam can be understood if the ejected nucleon comes from an S level near the top of the occupied level distribution. This interpretation of experimental results on Rh_{45}^{103} and $Ag_{47}^{106,109}$ supports the occurrence of an occupied $2s$ level close to $1g_{9/2}$ and $2\ p_{1/2}$ at $Z=45$ and 47 as suggested by the central elevation shell model. In the same way, the angular distributions of fast neutrons from the γ, n reaction on Bi and W isotopes require an s level near the top of the occupied level distribution in the range $N\sim108$–126. This suggests a continued rise of the $2s$ level above $1h$, $2f$, and $1i$, after the closing of the neutron shell at $N=82$, in accordance with the postulates of the central elevation model. Another point of interest is the large increase in the theoretical cross section produced by a substantial central elevation in the potential well (69).

Configuration Interaction and Shell Structure

Some basic questions raised by the success of shell model considerations are discussed by Weisskopf (70) in a qualitative comparison of the independent particle and strong interaction approximations [cf. Elsasser (70a)]. The analogy with an electron in a metal is used to illustrate the point that the mean free path of an intranuclear particle is strongly influenced by the operation of the exclusion principle. The short mean free path of a captured particle in a compound nucleus is associated with the availability of many nearby unoccupied levels into which the particle can be scattered. At the other extreme, a nucleon forming part of a degenerate gas of equivalent particles moves comparatively freely because of the absence of unoccupied nearby states.

Whether or not these considerations are adequate to account for the usefulness of the independent particle approximation depends on the nature (largely unknown) of the forces responsible for nuclear binding. The inadequacy of short range two-particle forces seems fairly well established. Many calculations have shown in detail how such forces strongly couple configurations differing by one or two orbitals (71, 72). Whether such forces can account for both the magnitude and symmetry dependence of nuclear binding energies is also in question (72a).

Schiff (73) has proposed a nonlinear meson theory to produce nuclear forces of a type compatible with the usefulness of the free particle approximation. It is described briefly as making the potential energy of a nucleon de-

pend primarily on the average nucleon density in its vicinity and relatively little on the positions of its immediate neighbors. This property insures weak coupling between configurations differing by a small number of orbitals. The possibility of strong coupling between remote regions of function space (differing by many orbitals) is perhaps not excluded, but such coupling is probably not incompatible with the apparent validity of the free-particle approximation for a small number of low states.

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ENERGY LEVELS OF LIGHT NUCLEI[1]

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The study of the energy levels of nuclei is essentially concerned with the location of the various stationary and quasi-stationary states characteristic of nuclear systems and the determination of the properties of these states. One pictures the stationary energy levels as representing arrangements of the nuclear constituents which are particularly preferred over other possible arrangements and which may exist for periods of time many orders of magnitude longer than the time required for a nucleon to traverse the effective dimensions of the nucleus. There is cause for hope that, by examining the distribution in excitation energy of such preferred arrangements and by studying their modes of formation and decay, one may eventually achieve an understanding of how nuclei are constructed and how the various particles within the nucleus interact. Clearly the matter is not simple: if it were not for the fact that both experiment and theory have been beset with perplexing difficulties, there would be little occasion for writing in 1951 a progress report on an art which had its inception in 1919.

The present discussion will be concerned only with the "light" nuclei, arbitrarily defined as the nuclei comprising 20 particles or fewer. At first glance, it may seem that the prospect of obtaining useful and unambiguous information on nuclear structure from the study of 10- or 20-particle systems is rather remote: much better, it might be thought, to concentrate either on heavier nuclei, where, because of the comparatively large number of particles involved, a statistical treatment may have some chance of success, or to devote attention exclusively to nuclei of two, three, or four particles where an explicit solution for the individual interactions might be feasible. Certainly both of these points of view have merit, and the active pursuit of these fields has in fact been very fruitful. Nevertheless, the light nuclei, as opposed to the "medium-to-heavy" or the "light, light" nuclei, offer quite fertile fields for exploration. On the one hand, the wealth of accessible energy levels in the light nuclei gives us an opportunity to use many different lines of attack and the opportunity to investigate facets of the problem which might never be revealed in the simpler two- or three-body systems; on the other hand, one may reasonably hope for simplifying features in 5- to 20-particle nuclei which would make unnecessary the surrender to a purely statistical treatment in which the nuclear constitutents lose their individuality. As support for the first point, it may be observed that nuclei of mass two, three, and four do not have, as far as is known, any excited stated of well-

[1] This review written in January, 1951 is principally a survey of papers published or in process of publication in 1950.

defined energy at all.[2] Although an atomic spectroscopist might find many things of interest in the hydrogen atom, his efforts to elucidate its structure would be severely limited if it had no line spectrum! Nuclei of mass five, six, and seven appear each to have one or two sharp states and from mass eight on, with a few exceptions, many states are known. In the 30-odd nuclei of mass of 5 to 20, over 200 energy levels have been identified, and it is not unreasonable to believe that many more will be found with further investigation.

Such a wealth of energy levels may not seem an unmixed blessing; if these actually represent different possible arrangements of all the constituents of these nuclei, we are confronted with a situation virtually impossible of analysis. The hope to which we cling—not entirely unjustified as we shall see—derives from a faith in the essential simplicity of nature: if, in the modest degrees of excitation with which we are concerned, the main body of the nucleus remains comparatively inactive, and only one or two particles are disturbed, we may still be able to formulate an analytical description of the events we observe, without resorting to statistical methods. Almost from the start, it has been assumed that the α-particle configuration, or groups of such configurations, would be essentially inactive in a moderately excited nucleus, suggesting that nuclei of odd mass number might reasonably be expected to be analogous to alkali or halogen atoms. In the case of the shell model, in which closed shells occur at 4, 16, and 20 nucleons, the number of active particles in an intermediate nucleus may be somewhat greater, and we may expect the interactions of these particles to have a significant bearing on the energy levels. Such effects, which in the atom are usually second order corrections to the predominant influence of the strong central field, may be of first order in the nucleus, where the active particles themselves make the major contribution to the field. Even so, the tendency of nucleons to form symmetric sub-groups may still restrict the number of variables to a manageable magnitude. Whether such simplifying assumptions are appropriate or not can, of course, only be determined by experiment, and until reasonably complete and reliable information on the location of energy levels in the nuclei of interest is obtained, even this simple question cannot be answered definitively.

As one examines the data available, one is struck by the comparatively large regions which for one reason or another have still not been adequately investigated: certain energy ranges of certain nuclei have been covered in great detail—other regions, less accessible to available techniques, have not been studied at all, and a considerable class of intermediate cases exists in which the present information is either insufficiently precise or quite ambiguous. Even among the low-lying levels, which should be the most decisive for

[2] The singlet interaction between the neutron and proton is sometimes described as an "excited state" of the deuteron, but the application of the term here is not unambiguous; there is evidence for a state in the α-particle at about 25 M.e.v., but the breadth is probably of the order of several M.e.v.

a theory of nuclear structure, many conspicuous gaps exist. The filling of these gaps has been a major point of attack during the past few years, and the success of the campaign is attested by the fact that the number of reasonably well-established levels below ten million volts excitation has doubled since 1948. There can be no question that many more levels are still to be located, but at least it may be said that the broad outlines of a comprehensive map of the energy levels is well under way for some of the light nuclei and that we may soon expect to be able to answer some of the questions raised by the theories.

The comparatively rapid advances which have occurred in the past few years are, understandably enough, closely associated with major improvements in technique. Because of the variety of problems confronting the nuclear spectroscopist, almost any new technique or improvement in technique indirectly makes accessible entirely new fields for study. The range of excitation energies within which well-defined energy levels occur in the light nuclei is in excess of twenty million electron volts; depending upon their individual properties, these levels may decay by charged particle emission, neutron emission, or γ-radiation, and often all three occur for a single level. To study particular energy levels we must be prepared to furnish excitation energies of the order of millions of volts and to detect disintegration products of several, not always easily distinguishable, kinds. The feasibility of systematically investigating the whole of the range where excited states are to be found depends then very intimately upon the development of quite specialized instrumentation.

In order to produce a given state of excitation in a specific nucleus, one often uses the expedient of producing the nucleus artificially, by combination of two lighter nuclei. Thus, for example, N^{14} can be produced by bombardment of C^{13} with protons. The mass defect of N^{14} with respect to these two constituents is 7.540 M.e.v.,[3] so by varying the kinetic energy of the protons, one can study systematically the region of excitation energies of N^{14} from 7.54 M.e.v. to an upper limit determined by the maximum proton energy available. Concomitant reactions involving C^{12} are easily eliminated by using isotopically enriched targets. The levels thus formed may decay by γ-radiation (they have in this particular case no other recourse except re-emission of the proton, which also occurs), and their location is indicated by maxima in the yield of γ-rays, measured as a function of bombarding energy. Since some of these levels are quite sharp—a few kilovolts or less in width—one needs a source of protons of quite accurately known energy, continuously variable over a wide range. Considerable attention has been given to the problem of producing accelerating and analyzing apparatus with the required characteristics, and now many installations exist which are capable of producing well-collimated beams of charged particles up to two or three million

[3] The masses used throughout this article are based upon tables compiled from reaction Q values recently determined in several laboratories. I am much indebted to Mr. C. W. Li for making the tables available in preliminary form.

volts with an energy spread of less than a kilovolt; a few installations are operating at even higher voltages with comparable homogeneity.

With the availability of bombarding particles with continuously controllable energies up to several M.e.v., one may hope greatly to extend the regions which can be systematically searched by the observation of excitation functions. An interesting example occurs in N^{14}: the bombardment of C^{12} by deuterons results in the formation of excited states of N^{14} in a somewhat higher range than does the addition of a proton to C^{13}, since the combination $C^{12}+H^2$ is 10.26 M.e.v. heavier than N^{14}. By studies of the yields of various products (γ-rays, protons, and neutrons), an accurate, and perhaps exhaustive, map of the major levels has been obtained from 11 to 13 M.e.v. in N^{14}, leaving a gap from 9.5 M.e.v., until recently the highest known level exhibited in $C^{13}+H^1$, to 11 M.e.v. The gap has now been closed with the observation of the 11.05 M.e.v. level in the bombardment of C^{13} by 3.76 M.e.v. protons (1). With further exploitation of this technique, we may hope for a reliable map of N^{14} with uniform coverage from 8 M.e.v. to 13 M.e.v. or higher. Such systematic surveys, even if over limited regions, are extremely useful since they yield not only the locations of energy levels, but also their widths.

Still more detailed information on certain types of levels is obtained from examination of the yield of elastically scattered particles. Although the study of the scattering of α-particles provided the first proof of the existence of nuclei, and many subsequent experiments have been done to elicit further information about the nucleus from the deviations from coulomb scattering of α-particles, only in the past few years has the method been extensively applied with protons. Within this period, the combination of well-collimated, monoenergetic proton beams and high resolution detecting equipment has made it possible to obtain accurate data on the variation of scattering with energy and angle of observation, which is of considerable aid in the assignment of spin values. The scattering of neutrons, again only recently brought to the stage where the necessary precision is obtainable, may be even more useful, since the absence of the interference of the coulomb scattering simplifies the analysis to some extent, although interference between resonant and potential sdattering must still be taken into account.

There exist in the nuclei of present interest a number of regions not otherwise directly accessible which can be reached by α-particle bombardment, where a detailed study both of the scattering and of the excitation functions of the various reactions would be most fruitful. Most of these regions have been surveyed by using α-particles from radioactive sources, but, because of the low intensities available, with inadequate resolving power. In only one or two cases have results been obtained with artificially accelerated α-particles of precision comparable with that obtained by other methods. It would appear that further exploitation of this technique is clearly indicated. The acceleration of tritons also permits investigation of quite new regions and is being pursued by several laboratories. He^3, which has been little used, should also make an interesting projectile.

The general methods of seeking energy levels by the excitation function

or elastic scattering methods just enumerated suffer from a serious handicap: the range of excitation which can be studied in the case of "compound" nuclei is limited on the low side by the binding energy of the bombarding particle in the nucleus under investigation. This energy averages, for protons and neutrons, around 7 M.e.v. and in some nuclei is considerably higher. For the lower levels, we must look to other techniques. In almost every nuclear reaction it is found that more than one state of the final nucleus is involved. In the case of the capture of a proton by C^{13}, for example, the state of N^{14} produced may radiate the excess energy in several quanta, representing transitions through several lower-lying states and finally to the ground state. Measurement of the energies of these successive γ-rays yields a portion of the "emission spectrum" of N^{14} and assists in locating the states between which transitions may occur. In a reaction in which disintegration into two particles occurs, as, for example,

$$B^{10} + H^2 \rightarrow (C^{12}) \rightarrow B^{11} + H^1,$$

the residual nucleus (B^{11}) frequently is left in an excited state and subsequently decays with radiation. Measurement either of the energies of the various associated proton groups or of the γ-ray energies then reveals the states in question. To some extent, which states are produced is accidental, since states of the residual nucleus may exist to which proton emission from the particular states in which the intermediate nucleus is formed is forbidden for one reason or another. However, if the bombarding energy is varied, one may presumably cover a sufficient range of states of the intermediate nucleus that all combinations are made possible. Generally speaking, one might expect that states of high spin would more often be discriminated against than states of low spin.

The measurement of particle groups and γ-rays associated with low-lying energy levels has been considerably refined in the past few years by the application of spectrographic techniques of high precision. Heretofore, almost all of our information on particle groups depended upon the measurement of ranges or ionization and suffered from the not inconsiderable uncertainties attendant upon these methods. Even the ground state groups, which are of vital importance in determining masses, have seldom been reliable to better than about 50 k.e.v., and great difficulties are encountered in resolving a distribution of any complexity. With the development of the magnetic spectrometer, it is now possible to improve the precision of the results by at least an order of magnitude and by making measurements at several bombarding energies, to identify positively the emitted particle and the target nucleus in each case. Among the many important results of such investigations has come a new appreciation of the importance of surface contamination of the targets in producing spurious groups and in introducing errors in energy determinations. An interesting by-product of this development is an entirely new technique for analysis of films only a few tens or hundreds of atoms thick.

Closely connected with our interest in the location of low-lying energy

levels is a curiosity about the radiative tranistions between them. In the past, the analysis of γ-radiation has been carried out by excessively tedious and disappointingly inaccurate cloud chamber techniques. Here again, the introduction of the magnetic spectrograph has effected a considerable improvement in our situation. By the use of thin converters and magnetic analysis of the resulting photoelectrons, Compton electrons, or pairs, we are now able to determine γ-ray energies with better than 1 per cent accuracy. In a number of cases, it has been possible to correlate level energies determined by particle group analysis and the corresponding γ-ray transitions to an accuracy of a few kilovolts.

It is unfortunate that the methods of magnetic analysis cannot be applied directly to neutron spectra. Except for the measurement of the energy of the recoil of the nucleus from which the neutron is emitted, which has been carried out in one or two cases, we must still rely on range measurements of proton recoils for information on neutron energies. Here the most useful detector has been the photographic emulsion. By counting large numbers of carefully selected tracks, it has been possible to obtain higher resolution than could be obtained by cloud chamber methods and to reduce by a large factor the time required to obtain a spectrum. The resolution is still, however, of the order of 100 or 200 kv. and the method is still rather tedious. A promising variant is the use of Li^6 loaded emulsions; observation of the α-particle and triton tracks resulting from the reaction $Li^6+n\rightarrow He^4+H^3$, again with careful selection of tracks, appears to make possible a resolution of 100 kv. or less for neutron energies near 1 M.e.v. (2).

Although we may say that, with techniques now available, we should in the not too distant future be able to specify the location of all the principal levels of the light nuclei over a fairly broad range of excitation energies, the question of determining spins, parities, and perhaps other important specifications of these levels remains an important problem. The principal method of attack up to this point has involved the measurement of the angular distribution of emitted particles or γ-rays with respect to the bombarding particles. In many situations, the results are complicated by the fact that more than one state is involved and the analysis does not yield a unique solution. With the application of short resolving time coincidence techniques and discrimination against irrelevant particles, it is possible to extract information of a much less ambiguous character. As a result of these developments, we now have, for the first time in the light nuclei, spin assignments of considerable reliability for several levels (see O^{16}, for example).

The present state of experimental information on the energy levels of the light nuclei is summarized in the diagrams on the following pages. On each diagram has been plotted on a vertical scale the locations of all the reasonably well-established levels up to about 10 M.e.v. with the excitation energies indicated. The estimated precision of the energy determinations is suggested by the number of significant figures in the entry: levels whose existence is doubtful are indicated by dashed lines. The binding energies of various par-

ticles[4] are entered on short lines just outside the main diagrams. In a few instances of particular interest, observed transitions have been indicated by arrows, vertical arrows representing radiative transitions, slanting arrows showing particle emission. In the interest of simplicity, the reactions through which the various levels are reached have been omitted; for the same reason, only a few references to the literature are cited in the discussion; for more detailed information and a more complete bibliography, the reader is referred to "Energy Levels of Light Nuclei, III," by Hornyak, Lauritsen, Morrison & Fowler (2a).

The diagrams and discussion have been presented in such a way as to exhibit a striking feature of the level structures: the apparent similarity of members of isobaric sets. To facilitate comparison, the isobars have been plotted together, with the ground states adjusted to correspond. Essentially this means that such mass differences as can reasonably be ascribed to pure electrostatic energy differences (and to the intrinsic mass difference between the neutron and the proton) have been subtracted. The observed ground state mass differences are indicated in parentheses on the diagrams. The similarity in the spacing of excited states is particularly clear for certain of the odd mass-numbered pairs, the "mirror nuclei," and is present to some extent in members of the even-numbered triads. This correspondence, if general, has a profound bearing on our ideas of nuclear structure and internucleon forces. If, for example, we consider two odd-numbered nuclei which differ only in the exchange of a single neutron for a proton (e.g.: Li^7 which has four neutrons and three protons, and Be^7 which has three neutrons and four protons), we might reasonably expect that the only difference in structure would lie in that some neutron-neutron bonds have been substituted for proton-proton bonds: all interactions between unlike particles are identical in the two cases. In particular, if the intrinsic nuclear forces between two neutrons and two protons are the same, the masses of the two nuclei should differ, in first order, only by the increased electrostatic energy associated with the binding of a proton and by the intrinsic proton-neutron mass difference (3) (0.782 M.e.v.). Such specifically nuclear properties as spin and parity should be unchanged. Comparison of the measured mass differences of the known odd isobars has shown that this is indeed the case, within the fairly large uncertainty of the electrostatic energy calculations; such differences as do appear may be accounted for, at least qualitatively, by the effects of near-instability in increasing the effective size of one of the nuclei and decreasing the coulomb contribution (4). In no case do we have among the light nuclei direct measurements of the spins of both members[5] (one is always radioactive), but the indirect evidence from studies of the β-decay is not in conflict with the assumption of equal spins. The situation of the respective

[4] Although these particles are indicated as p, α, and d for the proton, α-particle and deuteron respectively, the masses used are those of the complete atoms involved, as H^1, He^4, and H^2.

[5] Except the "light, light" $H^3 = He^3 = 1/2$ and $n^1 = H^1 = 1/2$.

excited states has been more troublesome: only in the last year or so have corresponding excited states in mirror nuclei been found and accurately measured in a sufficient number of cases to give any reasonable confidence in the validity of the theory (see, for example, B^{11}–C^{11}), and even among these have occurred some puzzling discrepancies which for a time gave rise to considerable consternation. Plausible explanations of these effects have now been advanced, and one may now say that the major inconsistencies have been removed (see Li^7 and C^{13}).

With some evidence at hand for the belief that specific neutron-neutron and proton-proton forces are indistinguishable in the nucleus, we may be emboldened to inquire whether neutron-proton forces are not also the same. Here we have a complication in that we are dealing with unlike particles, so that we may have more than one kind of interaction. As a consequence of the exclusion principle, two neutrons or two protons can exist in the same spatial state only if they have oppositely directed spins: for the neutron-proton interaction, however, the configuration in which the spins are parallel is also allowed. It may be expected then, that of a set of even mass-numbered isobars, the nuclide which has an equal number of protons and neutrons will be permitted many more states than its neighbors, which have paired identical particles. On the other hand, all states which do occur in the asymmetric members should have mates in the symmetric one. As regards the relative energy of the corresponding states, evidence from neutron-proton and proton-proton scattering experiments indicates that, at least in the ^1S interaction (antiparallel spins, zero relative angular momentum), $n-p$ and $p-p$ forces are indeed the same (5), aside again from the coulomb forces. These arguments would suggest, for example, that in the isobaric triad Be^{10}, B^{10}, C^{10}, having respectively $4p\ 6n$, $5p\ 5n$, and $6p\ 4n$, the first and last should correspond as mirror nuclei do and that their states would have analogues in B^{10}, with energies differing only because of (approximately calculable) electrostatic effects. In particular, some excited state of B^{10} should bear a close relation to the ground state of Be^{10} and C^{10}. Some evidence that this is so has come to light within the past two years in studies of both the mass 10 triad and the mass 14 triad (6). Three other such groups have been completed by the discovery (7) of B^8, N^{12}, and Na^{20}, whose ground states, at least, appear to bear the expected relation to Li^8, B^{12}, and F^{20}, respectively: the corresponding states in the center members have not been identified. In a few instances some higher states can be plausibly associated, but the evidence is still far from complete.

Energy Levels of the Odd Isobars

He^5-Li^5.—He^5 is unstable with respect to neutron emission, Li^5 to proton emission. Direct evidence for the existence of a state of He^5, presumably the ground state, occurs in the observation of a homogeneous α-particle group (width $\sim$0.14 M.e.v.) in the reaction $Li^7(d, \alpha)He^5$ [6] and the observation of a

[6] An abbreviation for $Li^7+H^2\rightarrow(Be^9)\rightarrow He^4+He^5$: the symbol for the compound nucleus, and sometimes that for the residual nucleus, is omitted for brevity. The

homogeneous proton group (width ~0.2 M.e.v.) in the reaction $He^4(d, p)He^5$. Reduced to center of mass coordinates, the width of the ground state appears from this data to be ~0.25 M.e.v., giving a mean life of $\sim 3.\times 10^{-21}$ sec. More recent measurements of the α-particle spectrum from $Li^7(d, \alpha)$ suggest that the state may be considerably broader, ~1 M.e.v. or more (8). The reaction energy (Q) of ~14.5 M.e.v. locates the ground state at ~0.6 M.e.v. above He^4+n. There is an indication of a second, broad, α-particle

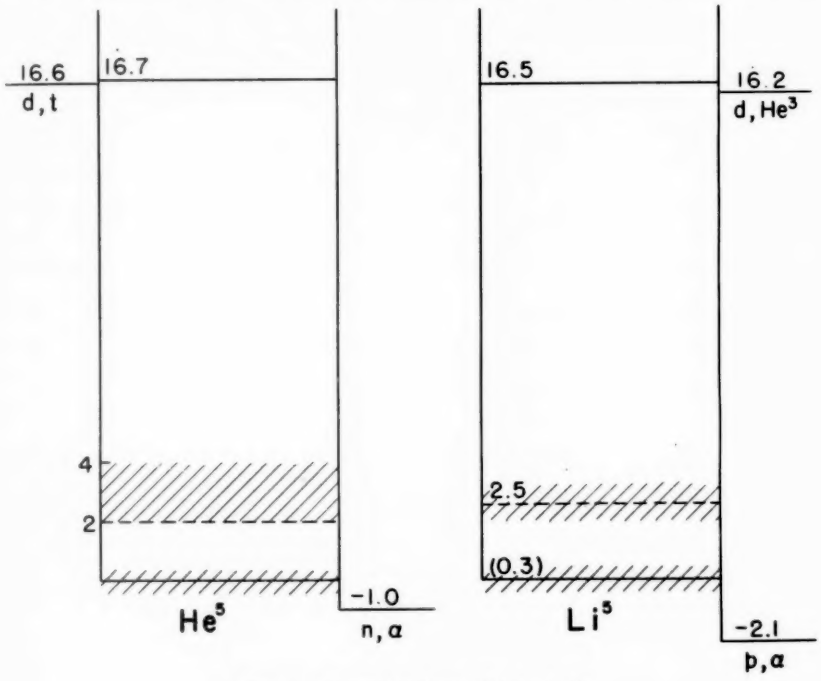

FIG. 1. Energy levels of He^5 and Li^5.

group corresponding to a level in He^5 at ~2 M.e.v. (9). Measurement (10) of the angular correlation in $Li^7(d, \alpha)He^5(n)He^4$ indicates that the ground state does not have spin 1/2.

Analysis of neutron scattering in He^4 indicates $P_{3/2}$ for the ground state,[7] at 1.0 M.e.v. above He^4+n, with a width ~1.1 M.e.v.; in addition, a $P_{1/2}$ state 3 to 4 M.e.v. higher seems also to be required (11). A state of Li^5, presumably the ground state, appears in the proton scattering in He^4. The

subsequent breakup of the residual nucleus, if breakup occurs, may be represented, for example, as He^5 $(n)He^4$. An excited state is indicated by an asterisk.

[7] The use of the Russell-Saunders notation for nuclear states is an approximation only; actually only the total angular momentum and the parity are regarded as good quantum numbers. The indicated value of "L" represents only the most prominent term: other values of orbital angular momentum are often mixed in to an appreciable extent.

analysis is not unique, and two solutions appear: a regular doublet with the ground state, $P_{1/2}$, at 1.8 M.e.v. above He^4+H^1 and the $P_{3/2}$ state 0.9 M.e.v. higher. The other solution indicates a $P_{3/2}$ ground state at 2.1 M.e.v. above He^4+H^1 and the $P_{1/2}$, 3 to 4 M.e.v. higher (11, 12). Observation of the reaction Li^6 $(\gamma, n)Li^5(p)He^4$ places the ground state at 1.6 ± 0.2 M.e.v. above He^4+H^1 and indicates an excited state at 2.5 ± 0.5 M.e.v. higher (13). We have chosen the value (2.1 M.e.v. $+H^1+He^4$) for the ground state of Li^5 to compare with the value (1.0 M.e.v. $+n^1+He^4$) for He^5 since these two quantities come from similar experiments. The difference $Li^5-He^5=0.3$ M.e.v. indicates a coulomb energy difference of 1.1 M.e.v. which may be compared

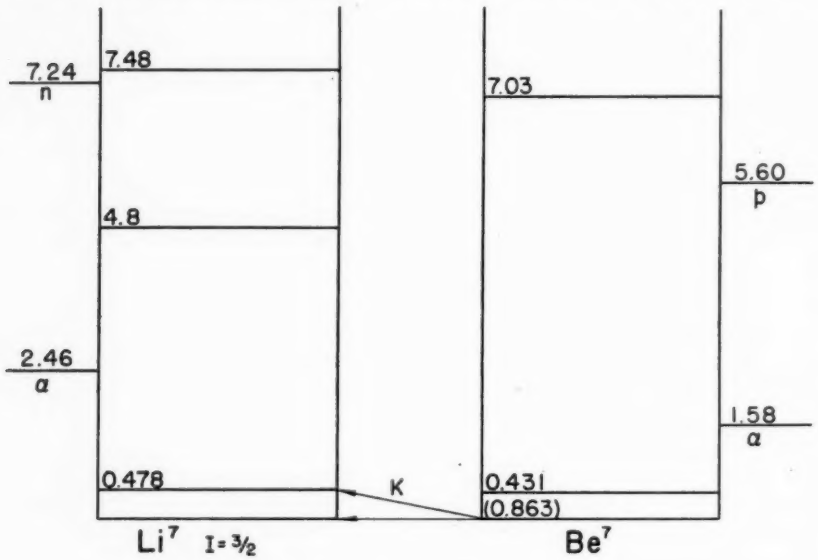

FIG. 2. Energy levels of Li^7 and Be^7.

with the value 1.4 M.e.v. estimated from the (admittedly crude) uniform model.

Resonances in the reactions $H^2(t, \alpha)n$ and $H^2(He^3, \alpha)H^1$ may be associated with levels at 16.7 M.e.v. in He^5 and at 16.5 M.e.v. in Li^5, respectively; no other levels are known.

Li^7-Be^7.—The first excited state of Li^7, at 478 ± 3 k.e.v., has been known since 1936; the corresponding state in Be^7, at 430 k.e.v., was first identified (14) in 1949. Both levels occur in several reactions: the first in Be^9 (d, α), $Li^6(d, p)$, $B^{10}(n, \alpha)$, $Li^7(p, p')$,[8] $Li^7(\alpha, \alpha')$, and in the decay (by electron capture) of Be^7; the second in $B^{10}(p, \alpha)$, $Li^6(d, n)$ and $Li^7(p, n)$. It is generally believed that the ground state and first excited states form components of an inverted $P_{3/2}-P_{1/2}$ doublet in each case, although the evidence is not

[8] Inelastic scattering of protons by Li^7.

conclusive. A spin value of 1/2 for the 478 k.e.v. state of Li^7 is indicated by the isotropy of the γ-radiation in $Li^7(p, p')$ and by the absence of correlation between the α-particles and γ-ray from $B^{10}(n, \alpha)$. On the other hand, it does not appear to be possible with a spin of 1/2 to account for the branching ratios observed in $B^{10}(n, \alpha)Li^7$, Li^{7*} and the angular distribution (15) of short range protons in $Li^6(d, p)Li^{7*}$. The depression of ~50 k.e.v. of the corresponding state in Be^7 can be accounted for partially in terms of the difference in the Thomas precession and magnetic spin orbit interactions in the two cases and partially as an effect of the expansion of the excited Be^7 nucleus (16). The ground state energy difference of 0.863 M.e.v. is about 20 per cent

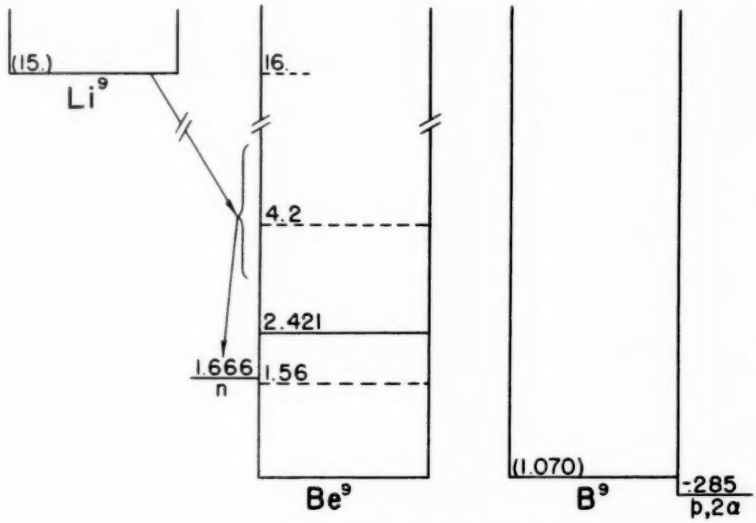

FIG. 3. Energy levels of Li^9, Be^9 and B^9.

lower than would be expected from the coulomb energy,[9] again suggesting an abnormally large effective separation of the protons in Be^7.

The assumption that the ground and first excited states are the two components of a ^2P term is supported by the absence of further states in Li^7 to at least 2.5 M.e.v. A level at 4.8 ± 0.1 M.e.v. is observed (17) in $Li^7(d, d')$ and $Be^9(d, \alpha)$: the expected mirror state in Be^7 has not been identified [it might be observed as a threshold for slow neutron production in $Li^6(d, n)Be^7$]. A further state of Li^7 appears at 7.48 M.e.v., observed as a resonance in $Li^6(n, \alpha)$: the mirror state, at 7.03 M.e.v., has recently been identified in $Li^6(p, \alpha)$ and $Li^6(p, p)$.

Li^9-Be^9-B^9.—The variation with energy of the photodisintegration cross section of $Be^9[Be^9(\gamma, n)Be^8]$ and of the angular distribution of photo-

[9] $\Delta E = \Delta E_0 - (n - H^1) = 0.59[Z(Z-1) - Z'(Z'-1)]/A^{1/3} - 0.78 = 1.07$ M.e.v. expected difference between corresponding states.

neutrons suggests the existence of an S level at ~110 k.e.v. below the threshold (1.56 M.e.v. in Be^9) and a D state ~2.5 M.e.v. above the threshold (~4.2 M.e.v. in Be^9), if the ground state is assumed to be $^2P_{3/2}$. The transitions indicated (18) are $P_{3/2} \rightarrow S_{1/2}$ and $P_{3/2} \rightarrow D_{5/2}$. A level at 2.4 M.e.v. is observed both in B^{11} (d, α) Be^9 and in the inelastic scattering of protons or deuterons by Be^9. Results from the former reaction give a level energy of 2.421 ± 0.005 M.e.v. and a width of <5 k.e.v. (19). No other levels appear in

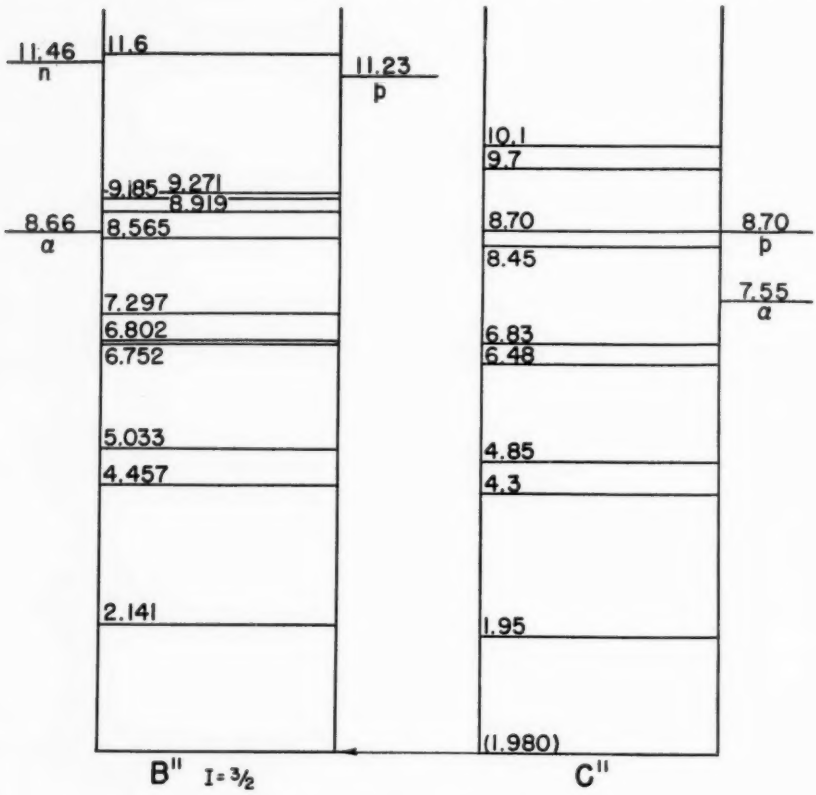

FIG. 4. Energy levels of B^{11} and C^{11}.

this work from 0 to 4.9 M.e.v. in Be^9; it is not clear why the postulated S and D levels should not have been detected. The region from 5 to 17 M.e.v. has not been investigated.

B^9, produced in the reaction $Be^9(p, n)B^9$, is unstable to proton emission, presumably decaying to Be^8+H^1 (0.2 M.e.v.) or $2He^4+H^1$ (0.3 M.e.v.); the width of the ground state is <0.13 M.e.v., corresponding to a mean life of $>5\times10^{-21}$ sec. No evidence is found for excited states <1.8 M.e.v., which is the limit of present investigations.

Li^9, which should lie ~15 M.e.v. above Be^9 according to Barkas' estimate (20) has been reported (21) produced in the reaction $Be^9(d, 2p)Li^9$. It decays with a half life of 0.175 sec. by electron emission to an excited state of Be^9 which further decays by neutron emission. Since Li^9 (three protons, six neutrons) has an excess of like particle pairs the ground state is not analogous to that of Be^9, but rather should correspond to some high excited state of Be^9. Subtraction of the coulomb energy difference and the intrinsic $n-H^1$ mass difference locates this expected state at ~16 M.e.v.

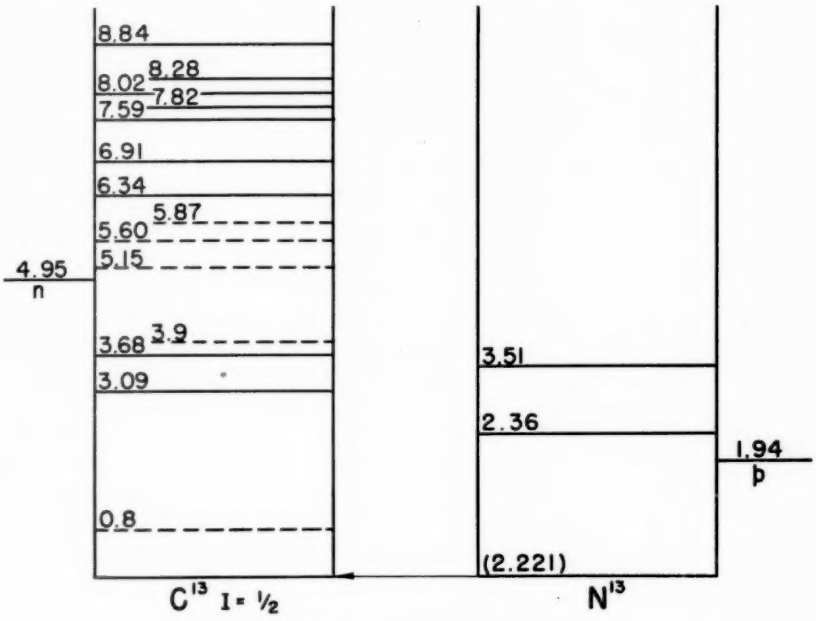

FIG. 5. Energy levels of C^{13} and N^{13}.

B^{11}-C^{11}.—The four groups of levels indicated in B^{11} from 2.1 to 9.3 M.e.v. have been identified by magnetic resolution of proton groups from $B^{10}(d, p)B^{11}$. The values are believed to be accurate to <10 k.e.v. (19). The first three groups of levels are also observed in the inelastic scattering of protons by B^{11}, but only the group around 7 M.e.v. has been resolved and this only into two components. Levels at 8.92, 9.18, 9.27 have also been observed (22) in the reaction $Li^7(\alpha, \gamma)B^{11}$. The region between 9.5 and 11.5 M.e.v. does not appear to have been explored adequately.

The levels indicated below 9 M.e.v. in C^{11} are observed in the neutron groups (23) from $B^{10}(d, n)C^{11}$. The lowest of these has been observed by several other investigators, and groups corresponding to levels at ~4.5 and 6.7 M.e.v. have been tentatively identified in earlier work. Levels at 9.7 and 10.1 M.e.v. are observed in the reaction $B^{10}(p, \alpha)Be^7$. Capture radiation of

9.46 M.e.v. energy is observed in $B^{10}(p, \gamma)C^{11}$ at a bombarding energy of 1.16 M.e.v., but the excitation function is not known.

C^{13}-N^{13}.—There have been recurring reports (24) of a level of C^{13} at 0.8 to 1.0 M.e.v., observed in $C^{12}(d, p)C^{13}$ and $B^{10}(\alpha, p)C^{13}$, but the present evidence is inconclusive. The 3.09 M.e.v. level is well established from particle groups observed in $C^{12}(d, p)C^{13}$ and $N^{15}(d, \alpha)C^{13}$ and from γ-radiation, the former yielding values 3.098 ± 0.008 M.e.v. and 3.083 M.e.v., respectively and the latter, 3.09 ± 0.01 M.e.v. Measurement of the internal pair conversion coefficient indicates that the radiation is electric dipole. Observation of proton groups from $C^{12}(d, p)C^{13}$ at 7.9 M.e.v. bombarding energy yields the following levels (25): 3.11, 3.77, 3.90, 6.34, 6.91, 7.59, 7.82, 8.02, 8.28, 8.84 plus three uncertain levels at 5.15, 5.60, and 5.87 M.e.v. The doublet 3.77 to 3.90 is of particular interest, since if a corresponding doublet exists in the mirror nucleus, N^{13}, the separation is apparently less than 10 or 20 k.e.v. Only one of the components appears in $N^{15}(d, \alpha)C^{13}$, at 3.677 M.e.v. a group corresponding to a level at $\sim$3.9 M.e.v. cannot, however, be excluded (19).

The region from 4.9 to 6.1 M.e.v. in C^{13} has been carefully explored in investigations of neutron scattering by C^{12}: it is concluded that no levels exist in this region of width >5 k.e.v. On the other hand, a level at $\sim$5.7 M.e.v. is reported from $B^{10}(\alpha, p)C^{13}$ which may be related to the group of levels 5.1 to 5.9 M.e.v. classed above as doubtful. The existence of such levels would be somewhat embarrassing to the mirror nucleus picture since it seems reasonably certain that no corresponding levels appear in N^{13}.

The remaining levels, from 6.3 to 8.9 M.e.v. are substantiated in part by the complexity of the total scattering cross section curve for neutrons on C^{12}: at least three broad maxima appear in this region and the presence of others of lower intensity cannot be excluded.

Only two levels appear in N^{13}, at 2.36 and 3.51 M.e.v., both identified in $C^{12}(p, \gamma)N^{13}$, $C^{12}(d, n)N^{13}$ and in the elastic scattering of protons by carbon (26). The lower level has an observed width of 35 k.e.v. The great width suggests strongly that the state is formed by s-wave protons, in which case the nuclear width-without-barrier is $\sim$3.7 M.e.v. (27): the assumption of higher angular momenta for the incoming protons leads to implausibly larger nuclear widths. Further support for the assumption of s-wave protons comes from the observed isotropy of the radiation and from the character of the proton scattering. The excitation energy of the state corresponds closely to that of the 3.09 M.e.v. state in C^{13}, if account is taken of the fact that the present state is unstable with respect to proton emission (28).

The higher state, at 3.5 M.e.v., exhibits quite different properties, particularly with respect to proton scattering; also, the angular distribution of the capture γ-radiation is not isotropic (29), excluding the assumption of s-wave formation. The observed width is 74 ± 9 k.e.v. (from the capture reaction); there is no indication of any doublet character for the level except that the scattering data do not seem to admit of a simple interpretation in terms of a single level. The calculated shift suggests correspondence with the

3.68 M.e.v. level of C^{13}. Investigation of the elastic scattering up to 4.0 M.e.v. (5.6 M.e.v. in N^{13}) reveals no further levels (26).

C^{15}-N^{15}-O^{15}.—Excited states of N^{15} from 5.28 to 9.16 M.e.v., exhibited both in proton groups from $N^{14}(d, p)N^{15}$ and γ-rays from $N^{14}(n, \gamma)N^{15}$, are well substantiated (30) and the energies are probably reliable to <10 k.e.v. The region from 9.2 to 11 M.e.v. has not been carefully searched; above 11.30

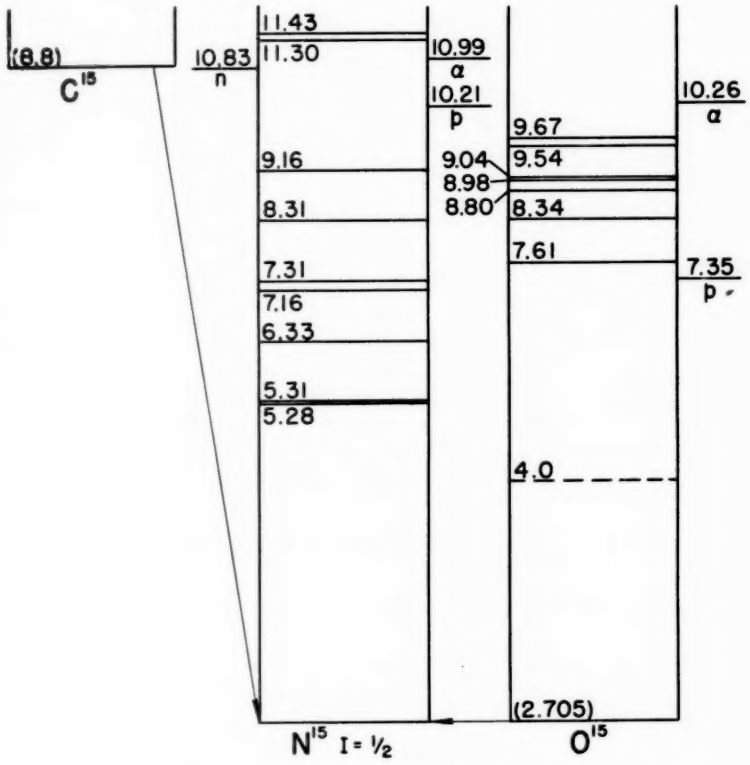

FIG. 6. Energy levels of C^{15}, N^{15} and O^{15}.

M.e.v., a number of levels is known from the reactions $N^{14}(n, p)C^{14}$, $N^{14}(n, \alpha)B^{11}$, and $C^{14}(p, n)N^{14}$.

A level at 4.0 M.e.v. in O^{15} reported from the reaction $N^{14}(d, n)O^{15}$ is in some doubt. From 7.61 to 9.67 M.e.v. seven levels, superposed on a continuous rise, have been observed in $N^{14}(p, \gamma)O^{15}$. The region from 5 to 7.5 M.e.v. deserves more investigation.

C^{15}, with a half life of 2.4 ± 0.3 sec. and a maximum electron energy of 8.8 ± 0.5 M.e.v., has been produced (31) in the reaction $C^{14}(d, p)C^{15}$. The state of N^{15} analogous to the C^{15} ground state would be expected to lie at $\sim$10.9 M.e.v.

O^{17}-F^{17}.—The levels indicated by solid lines on the O^{17} diagram have all been identified in both reactions $O^{16}(d, p)O^{17}$ and $F^{19}(d, \alpha)O^{17}$ with the exception of the three uppermost (8.0 to 9.0 M.e.v.) which for energetic reasons have been seen only in the latter reaction (25). There is some uncertainty as to the existence of a level at 1.6 M.e.v. (32). Levels at 4.56, 5.09, 5.37, 7.5, and 8.3 M.e.v. are also observed in the neutron scattering by oxygen (33):

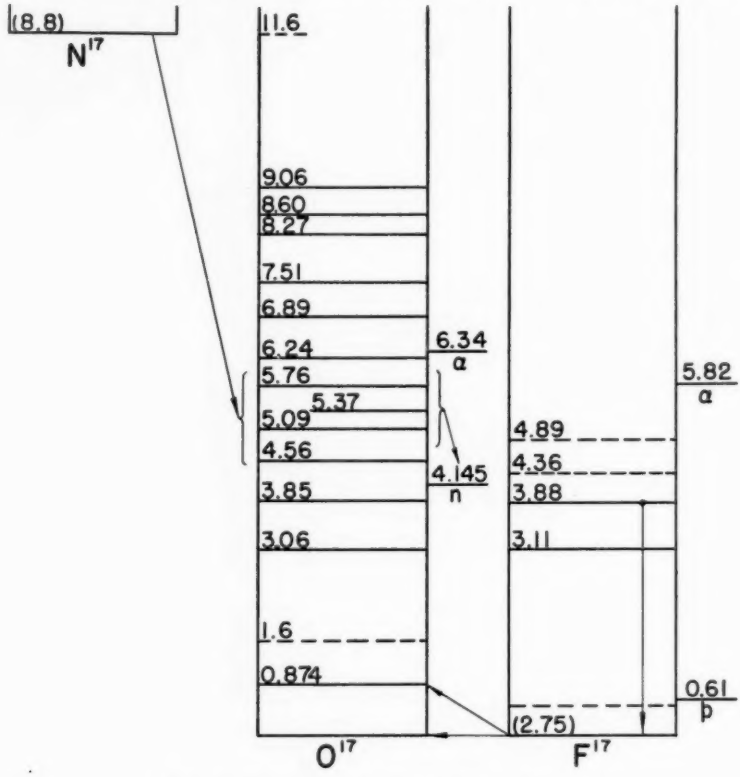

FIG. 7. Energy levels of N^{17}, O^{17} and F^{17}.

the first three of these have spin 3/2. Analysis (34) of the angular distribution of protons in $O^{16}(d, p)O^{17}$ indicates that the ground state is $D_{3/2}$ or $D_{5/2}$ and that the first excited state has the character $S_{1/2}$.

The elastic scattering of protons by O^{16} indicates levels in F^{17} at 3.11, 3.88, 4.36 (?), and 4.89 (?) M.e.v.: the 3.88 level is less than 3 k.e.v. wide and also appears as a resonance for capture γ-radiation (35). A considerable background appears at low energies, attributed to a bound $S_{1/2}$ state, presumably the mirror of the 0.87 M.e.v. state of O^{17}. It is to be expected that the state will lie considerably lower in F^{17} because of the effect of the low binding energy of the proton in modifying the boundary conditions at the

nuclear surface. Analysis of the resonances (35) yields the following assignments: 3.11 M.e.v. state: $S_{1/2}$, 3.88 M.e.v.: $F_{7/2}$, 4.36 M.e.v. $D_{3/2}$ (?), 4.89 M.e.v.: $P_{3/2}$ (?). Evidence from the γ-radiation suggests $D_{5/2}$ or possibly $D_{3/2}$ for the ground state of F^{17}.

The decay of F^{17} proceeds to the ground state (66 per cent) and to the first excited state (33 ± 5 per cent) of O^{17} with *ft* values of 3,240 and 350 sec., respectively (36). The very small value of the latter would suggest a much

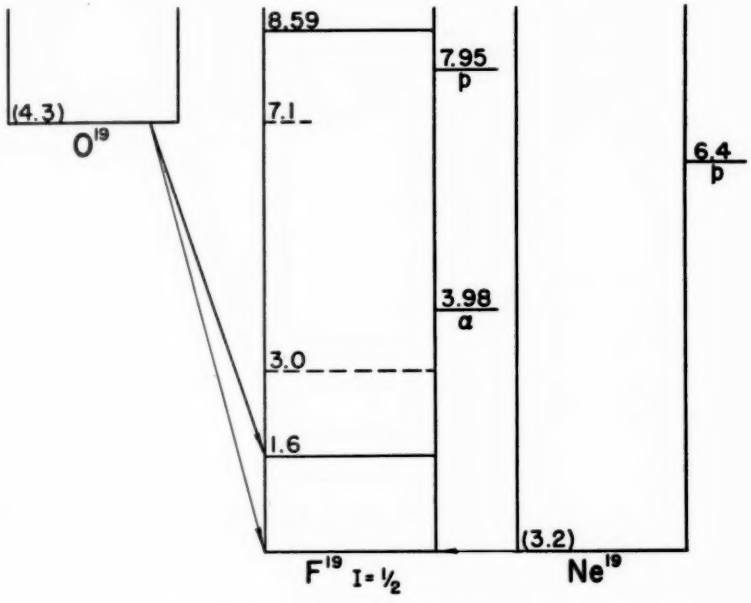

FIG. 8. Energy levels of O^{19}, F^{19} and Ne^{19}.

closer similarity of the ground state of F^{17} and the 0.87 M.e.v. state of O^{17} than appears from other evidence.

N^{17} decays by emission of electrons of maximum energy 3.7 ± 0.2 M.e.v. to states in O^{17} which are neutron unstable to the extent of about 1 M.e.v. The half life is 4.14 ± 0.04 sec. Subtraction of the coulomb and $n-H^1$ energy difference places the expected analogue state at $\sim$11.6 M.e.v. in O^{17}.

O^{19}-F^{19}-Ne^{19}.—The 1.6 M.e.v. level of F^{19} has been identified in the β-decay of O^{19}, and in inelastic scattering of neutrons and of deuterons by F^{19}. A second state appears at 3.0 M.e.v. in the deuteron scattering (37). No further states are known below 8.59 M.e.v., where a resonance in $O^{18}(p, \alpha)N^{15}$ has recently been reported (38). Above 10.4 M.e.v. a large number of states has been resolved in the reaction $O^{18}(p, n)F^{18}$.

Ne^{19} decays by emission of 2.2 ± 0.1 M.e.v. positrons, with a half life of 20.3 ± 0.5 sec. The observed *p-n* threshold for production of Ne^{19} is consistent

with the assumption that the decay proceeds to the ground state of F^{19}. No levels of Ne^{19} are known.

O^{19} decays predominately (70 per cent) to the 1.6 M.e.v. state of F^{19}. The ground state transition yields a mass value of 4.1 to 4.5 M.e.v. above F^{19}. Correction for coulomb energy and $n-H^1$ difference locates the corresponding F^{19} state at ~7.1 M.e.v.

Energy Levels of the Even Isobars

He^6-Li^6-Be^6.—He^6 decays to Li^6, emitting electrons of maximum energy 3.215 ± 0.015 M.e.v., with a half life of 0.83 sec. The comparative half life

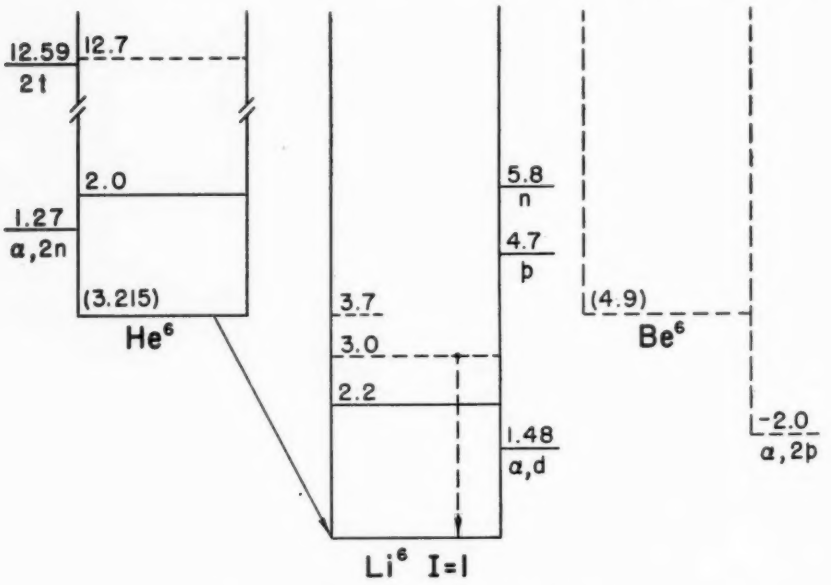

Fig. 9. Energy levels of He^6, Li^6 and Be^6.

(*ft*) of 590 sec. is consistent with the expected character $^1S_0$, even parity, for the He^6 ground state if Gamow-Teller selection rules apply (39). Using the estimated coulomb energy and n-H^1 difference, one finds that the corresponding spin zero state of Li^6 would lie at ~3.7 M.e.v. A level of Li^6 at 2.1 to 2.3 M.e.v. which has been identified (37) in the reaction $Li^7(d, t)$, and possibly in the scattering of α-particles in deuterium, would appear to lie too low to be identified with this state. Another level (or in view of the experimental uncertainties, possibly the same level) is suggested by the observation of ~3.0 M.e.v. γ-radiation in the bombardment of Be^9 with 2.5 M.e.v. protons. The high intensity of this radiation suggests that it follows particle emission and the reaction $Be^9(p, \alpha)Li^{6*}$ seems the most plausible explanation. If a γ-emitting level of Li^6 does exist in this region, the level must have $I=0$ and even parity in order to prohibit disintegration into He^4+H^2, which is

energetically possible above 1.5 M.e.v. It is tempting to assume that this is in fact the $^1S_0$ level which corresponds to the ground state of He^6, although the energy still appears to be too low. No other states of Li^6 have been identified. A state of He^6 at 2.0 M.e.v. has been observed (40) in the reaction $Li^7(t,\alpha)He^6$. There is some evidence for a state at 12.7 M.e.v., observed as a resonance in $H^3(t, 2n)He^4$.

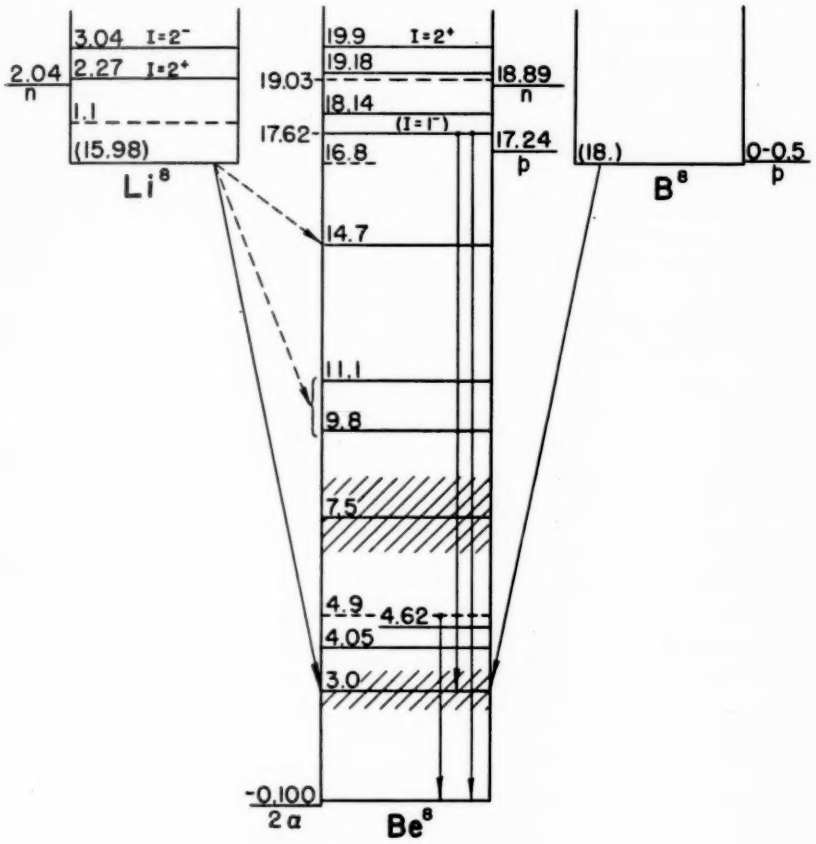

FIG. 10. Energy levels of Li^8, Be^8 and B^8.

From the mass of He^6, one may estimate that Be^6 should be about 4.9 M.e.v. heavier than Li^6, where it would be unstable by about 2 M.e.v. to disintegration into He^4+2H^1. It may be expected that the consequent large average proton separation may reduce the energy somewhat, but hardly to the point of stability (4). Be^6 has not been observed.

Li^8-Be^8-B^8.—Li^8 lies 15.98 M.e.v. above the ground state of Be^8: the decay proceeds mainly to a broad excited state at 3.0 M.e.v. and, with somewhat lower probability, to other broad states at ~10 and ~13 M.e.v.: all

three states subsequently decay by α-particle emission. No transitions to the ground state have been observed. B^8 is just stable with respect to proton emission, and has a mass $\sim 18 \pm 0.5$ M.e.v. above Be^8. The decay is similar to that of Li^8, involving at least the 3 M.e.v. level but again not the ground state (7).

Calculation of the coulomb energy differences indicates that the state of Be^8 corresponding to the ground state of Li^8 should lie at 17.0 M.e.v., while the ground state of B^8 would be expected to be at 18.6 M.e.v., and hence would be unstable with respect to proton emission. Since B^8 is in fact just stable, we must suppose again, as in the case of Be^6, that the loose binding of the last proton so modifies the conditions at the nuclear boundary that the total energy is reduced by ~ 0.5 to 1.0 M.e.v. In view of the fact that Be^8 is itself unstable to α-particle emission and, at 17.2 M.e.v. unstable to proton emission, the Li^8-B^8 ground state analogue might also be suppressed in Be^8, putting the state in the neighborhood of 16.5 to 17 M.e.v. The region in question has not yet been searched: such a state might, if it were not too broad, appear as a threshold for slow neutron production in $Li^7(d, n)$ at a bombarding energy of 2 to 2.6 M.e.v.

Above the ground state of Li^8, three levels are known, at 1.1, 2.3, and 3.0 M.e.v. The 1.1 and 2.3 M.e.v. states appear (37) in the reaction $Li^7(d, p)$, while those at 2.3 and 3.0 M.e.v. are observed (41) in neutron scattering by Li^7. The state at 2.3 M.e.v. is formed by p-wave neutrons and has $I = 2$, even parity; the 3.0 M.e.v. state, formed by s-wave neutrons has $I = 2$, odd parity. The analogue states in Be^8 would be expected to lie between 18 and 20 M.e.v. Actually several states have been identified in this region in reactions of $Li^7 + H^1$. The well-known level at 17.62 M.e.v. [441 k.e.v. resonance in $Li^7(p, \alpha)$] appears from the angular distribution of the γ-radiation to have $I = 1$, odd (42), although the proton scattering data would indicate $I = 1$, even (14, 43). Elastic proton scattering also indicates levels at 18.14 and 19.03 M.e.v. The level at 19.18 M.e.v. appears as a resonance in $Li^7(p, n)$ and one at 19.9 in $Li^7(p, \alpha)$. Analysis of the angular distribution of α-particles from the latter indicates $I = 2$, even and suggests a several M.e.v. broad level with $I = 0$, centered near 17 M.e.v.

Of the low lying states of Be^8, that at 3 M.e.v., which appears in many reactions, has received most attention. There is some suggestion that more than one level is involved (44) although the most recent work (45) indicates that, at least in the decay of Li^8 and in $B^{11}(p, \alpha)Be^8$, only one level, at 2.96 ± 0.06 M.e.v. with width 1.2 M.e.v., occurs. Further excited states at 4.05, 4.9, 7.5, 9.8, 11.1 and 14.7 M.e.v. have been identified in neutron groups from $Li^7(d, n)$: a 4.9 M.e.v. γ-ray indicates that at least one of these levels does not readily yield α-particles. A level at 4.62, possibly to be identified with one of the above, is reported in $Be^9(d, t)Be^8$.

Be^{10}-B^{10}-C^{10}.—Be^{10} decays to the ground state of B^{10} with the emission of 0.56 M.e.v. electrons, with a half life of 2.7×10^6 years. The long half life caused considerable perplexity in view of the general assumption that the

spins of Be^{10} and B^{10} were 0 and 1, respectively, until Goldhaber (46) in 1948 suggested that the spin of B^{10} might in fact be 3, a prediction which was immediately confirmed (47). C^{10}, presumably a spin zero nucleus, decays to an excited state, probably that at 0.72 M.e.v., of B^{10}, with a life time of 19 sec., indicating an allowed transition, and suggesting I = 1 for the 0.72 M.e.v. state. From the observed maximum positron energy, 2.2 ± 0.1 M.e.v. plus

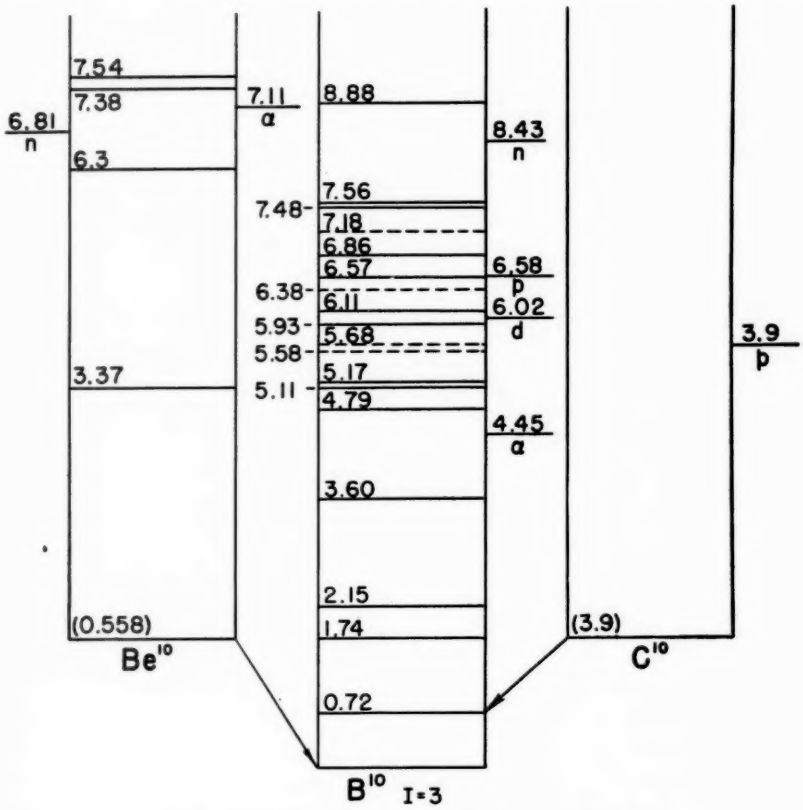

FIG. 11. Energy levels of Be^{10}, B^{10} and C^{10}.

the γ-ray energy 0.96 ± 0.2, the mass of C^{10} appears to be 4.2 ± 0.2 M.e.v. greater than that of B^{10}. If the γ-ray is in fact 0.72 M.e.v. the mass difference $C^{10} - B^{10}$ is 3.9 M.e.v.

From the coulomb energy differences, one estimates $B^{10*} - Be^{10} = 1.4$ M.e.v. and $C^{10} - B^{10*} = 2.0$ M.e.v., placing the analogue state, B^{10*}, at 1.9 to 2.0 M.e.v. (6). One may expect these estimates to be more reliable than those made for certain other triads, since here all three nuclei are quite tightly bound. Good evidence, from a neutron group observed in $Be^9(d, n)$, exists for

a level of B^{10} at 2.15 M.e.v. which may be the expected spin zero state. There has recently appeared evidence for an additional level at 1.79 M.e.v. which might equally well be the state in question (48). The apparent absence of the corresponding γ-ray transition to the ground state is consistent with the expected spin change of 3 and favors the latter interpretation, which also brings the higher levels into better agreement (see below).

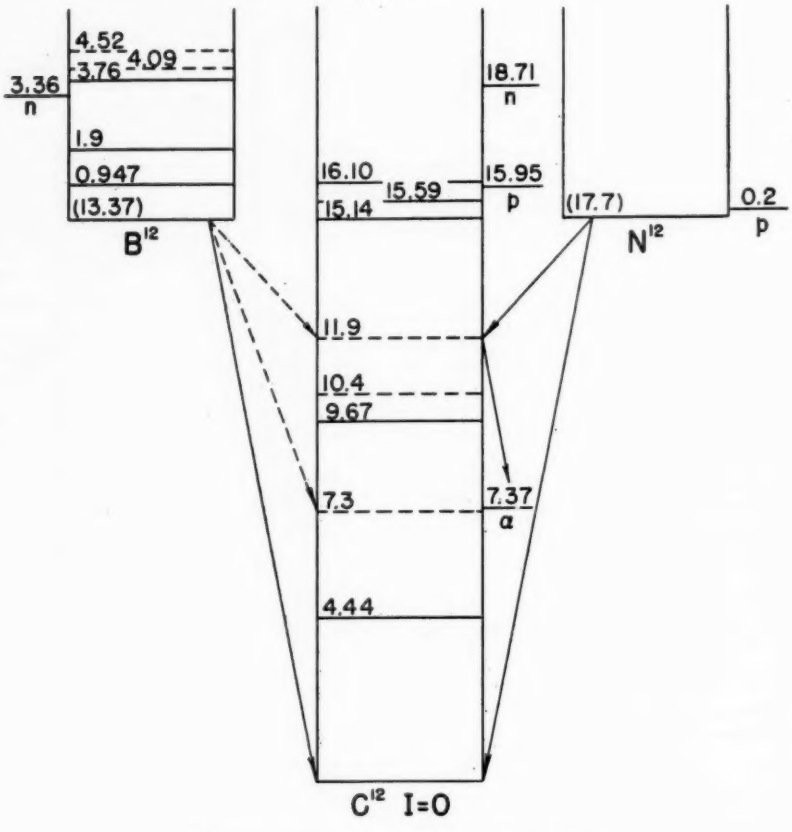

FIG. 12. Energy levels of B^{12}, C^{12} and N^{12}.

The present situation of the low lying states of B^{10} is not entirely clear. A number of γ-ray transitions has been observed in the reaction $Be^9(d, n)B^{10*}$, and the energies measured with considerable accuracy. The most plausible combination of this information with that obtained by observation of neutron groups results in levels at 717_{-5}^{+1} k.e.v., 1.74 ± 0.02 M.e.v., 2.15 ± 0.02 M.e.v., and 3.60 ± 0.03 M.e.v.: the γ-transitions observed are: 0.4, 0.7, 1.0, 1.4, 2.1, 2.8, and 3.6 M.e.v. Above 3.6 M.e.v., the following levels seem reasonably well established: 4.79, 5.11, 5.17, 5.93, 6.11, 6.57, 6.86, 7.48, 7.56, and 8.88 M.e.v. (48).

In Be^{10}, levels have been identified at 3.37, 6.3 (33), 7.38 (33), and 7.54 M.e.v.: a careful search for proton groups in $Be^{9}(d, p)$ reveals no levels <3.37 M.e.v. (49).

The comparative sparsity of levels in Be^{10} is a good illustration of the action of the exclusion principle in prohibiting certain types of levels in a system with excess like particles. On the other hand, as has been pointed out earlier, every level of Be^{10} should have a counterpart in B^{10}. For the first two

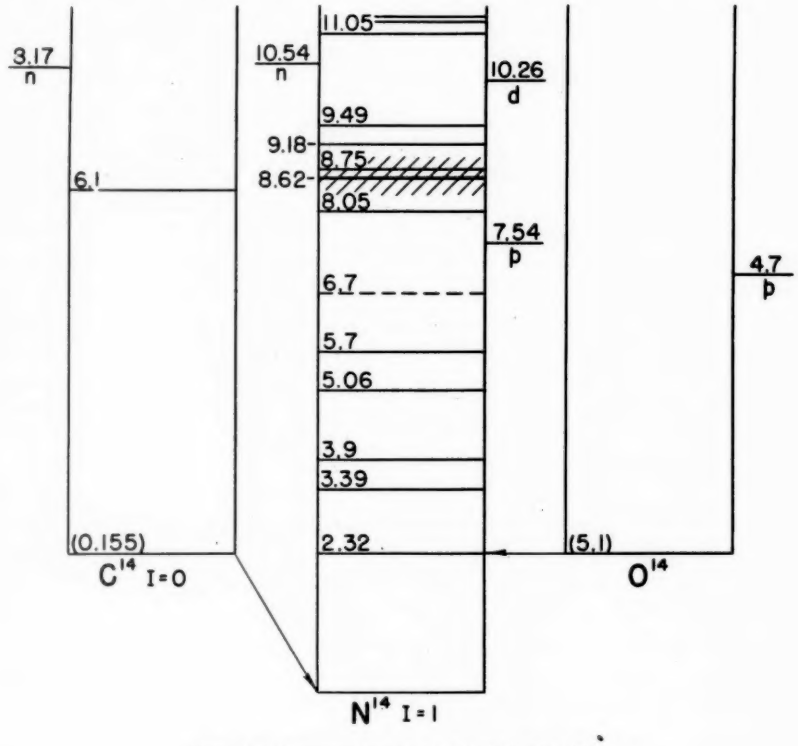

FIG. 13. Energy levels of C^{14}, N^{14} and O^{14}.

excited states, one may make reasonable associations (5 and 7.5 M.e.v. in B^{10}) but the upper pair (7.38 and 7.54) present a problem. The region immediately above and below 8.88 M.e.v. in B^{10} has been searched with some care in the $Be^{9}(p, n)$ reaction and appears only to contain the one level indicated, superposed on a slowly rising background (50).

B^{12}-C^{12}-N^{12}.—B^{12} decays through an allowed transition principally to the ground state of C^{12}; possibly 5 per cent of the transitions lead to levels at ~7 and ~11 M.e.v. Neither γ-radiation nor α-particle emission has yet been observed, although both are expected. N^{12} emits positrons, again mainly to the ground state of C^{12}, although delayed α-particles have been observed indicating decay to states >7.4 M.e.v. The energy of the α-particles (~4

M.e.v.) suggests that the state involved is in the neighborhood of 11 to 12 M.e.v. (7): a broad state at 11.9 M.e.v. is in fact observed (23) in $B^{11}(d, n)$.

The first order estimate of the coulomb energy difference yields $C^{12*}-B^{12}=1.8$, $N^{12}-C^{12*}=2.3$ M.e.v. (where C^{12*} indicates the mass of the expected analogue state). The observed difference N^{12}—$B^{12}=4.2$ M.e.v. agrees very well, although this agreement must be somewhat fortuitous in view of the expectation that the near-instability of N^{12} should decrease its coulomb energy (see, e.g., B^8). The analogue state of C^{12} should lie at ~15.2 M.e.v., and in fact a state at just this location has recently been identified (23). The observation that the state is relatively sharp is consistent with its expected $I=1$, even character, since α-emission to the ground state of Be^8 (presumed 0, even) would be forbidden and emission to a 2, even excited state of Be^8 would require d-wave α-particles. Another possible candidate is a state at 15.59 M.e.v. which is also sharp: the 16.10 M.e.v. state appears to have $I=2$, odd (from the observed γ-ray intensities in $B^{11}(p, \gamma)C^{12}$).

Levels in B^{12} have been identified at 0.947 ± 0.005, 1.91, 3.76 (33), 4.09 (?) and 4.52 (51) M.e.v. While the 0.95 M.e.v. level appears to match the 16.11 level of C^{12}, no other argument exists for suggesting a direct association. The region above 16.1 M.e.v. in C^{12} has not been adequately explored.

Lower lying levels of C^{12} have been identified at 4.44, 7.3, 9.67, 10.4, and 11.9 M.e.v. The level at 7.3 M.e.v. appears only weakly in several reactions (52), suggesting that it must be quite different in character from the ground state or the 4.44 M.e.v. state. There is some indication that the 7.3 level is actually a doublet (53).

C^{14}-N^{14}-O^{14}.—C^{14} decays to N^{14} with the emission of electrons of 155 k.e.v. maximum energy. The long half life of ~5,600 years is difficult to reconcile with the usual assumption that C^{14} and N^{14}, which have measured spins $I=0$ and 1, respectively, both have even parity. The spectrum has very nearly the allowed shape although there is indication of some curvature in the Fermi-Kurie plot (54). O^{14} decays by emission of 1.8 ± 0.1 M.e.v. positrons, followed by a 2.3 M.e.v. γ-ray, with a half life of 76.5 ± 2 sec. Subtraction of the coulomb effect and the $n-H'$ mass difference places C^{14} 2.32 M.e.v., O^{14} 2.5 M.e.v. above the ground state of N^{14}, suggesting that the 2.3 M.e.v. state of N^{14} observed in the O^{14} decay is the required analogue state (6). Good evidence for a state at 2.32 M.e.v. has appeared in the reaction $C^{12}(d, n)N^{14}$ through the observation of a neutron group and a corresponding γ-ray, and supporting evidence is afforded by the γ-radiation from $C^{13}(p, \gamma)N^{14}$. However, a rather considerable difficulty arises in the decay of O^{14} since the β-transition would be strictly forbidden ($I=0\rightarrow I=0$) under Gamow-Teller selection rules. The comparative half life ($ft=3{,}000$ sec.) places it clearly in the allowed class, suggesting a strong component of the β-interaction obeying Fermi rules, if the spin assignments are correct.

Other states in N^{14} at 3.39, 3.9, and 5.06 M.e.v. are fairly securely established from neutron groups (55) and γ-rays from $C^{13}(d, n)N^{14}$. A state at 5.7 M.e.v. is indicated by the γ-rays: the neutron group has not been observed.

Inelastic scattering of protons on nitrogen confirms the 5.06 M.e.v. level and indicates a level at ~6.7 M.e.v. Levels from 8.05 to 9.49 M.e.v., including a broad state at 8.62 M.e.v. (~0.6 M.e.v. wide) appear as resonances (56) in $C^{13}(p, \gamma)N^{14}$. The only certain state of C^{14} lies at 6.10 M.e.v. (57).

N^{16}-O^{16}-F^{16}.—Although the ground state of N^{16} is involved in several reactions, the mass remains rather uncertain, values from 9.7 to ~10.8 M.e.v. above O^{16} having been reported. The decay is complex, proceeding to the ground state of O^{16} (approximately 20 per cent) and to γ-emitting states from 6.1 to 7.1 M.e.v.; whether the pair emitting state at 6.05 M.e.v. is in-

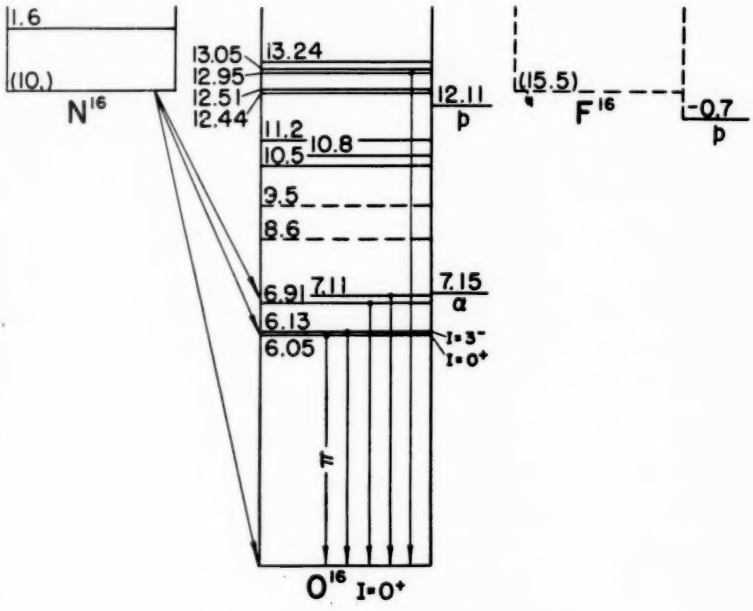

FIG. 14. Energy levels of N^{16}, O^{16} and F^{16}.

volved is not known. From the estimated coulomb energy and $n-H^1$ differences one expects the analogue state of O^{16} to lie in the neighborhood of 12.2 to 13.3 M.e.v.: several states, observed in the excitation function of $N^{15}+p$ are possible candidates. The same calculation places F^{16} at ~15.5 M.e.v. where it would be unstable against proton emission. That F^{16} is in fact unstable is suggested by its failure to appear in the bombardment of O^{16} with high energy protons (7).

The lowest excited state of O^{16} decays by the emission of nuclear pairs (the only example of such emission known), indicating a spin of zero, with even parity; the angular distribution, life-time and energy spectrum are all consistent with this picture. Investigation of the angular correlation of α-particles and 6.1 M.e.v. γ-rays from the reaction $F^{19}(p, \alpha)O^{16}$ indicates

I = 3, odd for the next state, at 6.13 M.e.v. Two other γ-emitting states, at 6.9 and 7.1 M.e.v. are observed in the same reaction. The region from 7 to 12 M.e.v. needs further exploration.

O^{18}-F^{18}-Ne^{18}.—In the mass 18 isobars occurs the first case in which the effect of the increasing coulomb energy is sufficiently great to cause the symmetric member to be unstable to β-decay. F^{18} decays to O^{18} by emission of positrons of 0.64 M.e.v. maximum energy. The comparative half life (*ft*

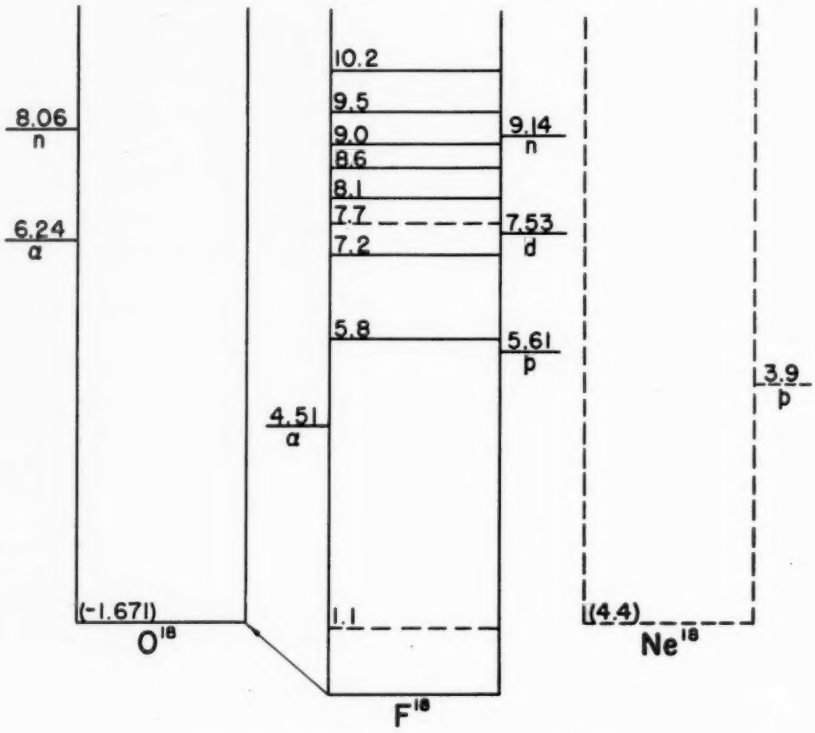

FIG. 15. Energy levels of O^{18}, F^{18} and Ne^{18}.

= 4,100 sec.) indicates an allowed transition, consistent with the assumed ground state assignments (I = 1, even → I = 0, even). The estimated coulomb plus $n - H^1$ energy difference F^{18*}-O^{18} is 2.8 M.e.v., placing the analogue state at 1.1 M.e.v. in F^{18}. A level at 1.1 M.e.v. has been reported (37), in the reaction $F^{19}(d, t)F^{18}$. Ne^{18}, which has never been observed, would be expected to lie about 4.4 M.e.v. above F^{18}.

Several levels from 5.8 to 10.2 M.e.v. in F^{18} have been identified in $N^{14}(\alpha, n)$, $N^{14}(\alpha, \alpha)$ and $O^{16}(d, p)$; the region below 6 M.e.v. has not been adequately searched.

F^{20}-Ne^{20}-Na^{20}.—F^{20} decays predominantly with the emission of electrons

of maximum energy 5.33 M.e.v. to an excited state of Ne^{20} at 1.64 M.e.v.: the ground state transition occurs with a probability ~3 per cent with an observed maximum energy of 6.7 M.e.v. (58). The analogue state in Ne^{20} is expected at 10.1 M.e.v. Na^{20} decays to an α-particle-unstable state of Ne^{20} in the region of 6.8 to 10.8 M.e.v.; whether transitions to lower states occur is not known. From the p-n threshold the mass of Na^{20} is given as 15.3 M.e.v. above Ne^{20}, or about 0.6 M.e.v. stable with respect to proton emission (7). Subtracting the coulomb and $n-H^1$ difference, the corresponding Ne^{20}

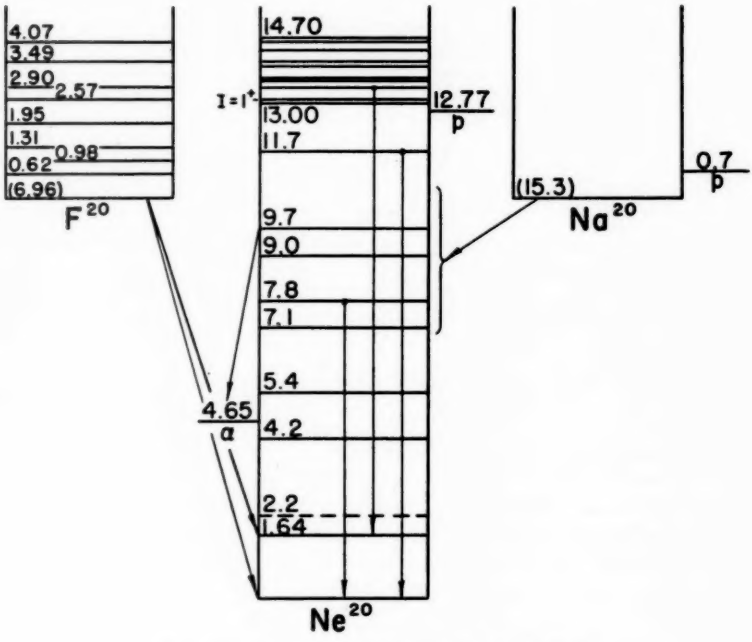

FIG. 16. Energy levels of F^{20}, Ne^{20} and Na^{20}.

state would be expected at ~11.7 M.e.v. which agrees only rather poorly with the estimate from F^{20}. The fact of the near-instability of Na^{20} suggests that the lower value is more reliable.

The experimental situation of the energy levels of Ne^{20} near 10 M.e.v. is not entirely clear. From neutron groups in the reaction $F^{19}(d, n)Ne^{20}$, states at 7.8, 9.0, and 10.1 M.e.v. (in addition to lower lying states at 1.5, 2.2 (?), 4.2, 5.4, and 7.4 M.e.v.) have been identified. Gamma rays from the same reaction appear at 8, 9.4, and 11.7 M.e.v. (59). Of these states, only one, at 9.7 M.e.v. appears to decay mainly by α-particle emission (32). In the scattering of α-particles by O^{16}, one report (60) indicates two levels with spin 1 at 9.0 and 10.1 M.e.v., while another (61) suggests a single level at 9.4 M.e.v. with $I=2$. The existence of many low-lying states of F^{20} suggests that the

corresponding region of Ne^{20} may be even more complex than it now appears.

Levels of Ne^{20} from 13.0 to 14.7 M.e.v. have been extensively studied in the reaction $F^{19}(p, \alpha)O^{16}$. In one case, for the level at 13.09 M.e.v. (0.340 M.e.v. proton energy), the angular correlation between α-particles and γ-rays fixes the assignment as $I=1$, even. One level, at 13.41 M.e.v., yields capture γ-radiation to the 1.64 M.e.v. state of Ne^{20}. Of the several levels which decay both to the ground state and the pair-emitting state of O^{16}, all show a decided preference for the latter, despite the unfavorable coulomb barrier and despite the fact that the spin changes are the same. This fact suggests that other unknown factors in the nuclear matrix elements may have a profound influence on the course of a given reaction (62).

Conclusion

It would appear from the foregoing survey of the known energy levels of the light isobars that the assumption of charge independence of the specifically nuclear forces must be a very good approximation to the true state of affairs within the nucleus, accurate to some few tens of kilovolts in the tens of millions of volts representing the total binding energies. Even these relatively small discrepancies can be satisfactorily accounted for in terms of effects which enter the picture in a natural way and whose magnitudes are quite reasonable.

On the other hand, the problem of accounting for the observed arrangement of energy levels remains unsolved. In a general way, it is possible to understand certain features of the p-shell nuclei (mass 5 to 16) by postulating a relatively strong spin-orbit coupling, but clearly other effects enter which may be more important in determining the order of even the low excited levels. It is obvious that much more experimental information is needed, particularly with respect to the spins of these states, before we are able to give an adequate account of the structure of the light nuclei.

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NUCLEAR MOMENTS[1]

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Introduction

Many important developments in the field of nuclear moments occurred during the year 1950. Not only were a number of new moments measured, but also quite a few new methods of measurement were proposed and developed. In addition, a number of new phenomena were discovered in the course of the measurements and many of these were successfully explained.

In order that the discussion of these many diverse developments may be simplified in the following pages, they will be somewhat arbitrarily classified as new methods of measuring nuclear moments, newly discovered phenomena associated with nuclear moment measurements, theoretical interpretations, and new moment measurements.

New Methods of Nuclear Moment Measurements

One of the most important developments of the year 1950 was the successful use of two precision methods of measuring the proton magnetic moment directly in terms of the nuclear magneton. Since all other nuclear magnetic moments are expressed in terms of the proton magnetic moment, these experiments fixed the scale for all nuclear magnetic moment measurements. In one of these experiments introduced by Sommer, Thomas & Hipple (103), the Larmor precession frequency of the proton magnetic moment is measured with conventional nuclear magnetic resonance techniques. Then in the same magnetic field the orbital frequency of a proton is measured by observing the frequency of an oscillating field that leads to an expansion of the orbit of a proton trapped in the magnetic field by means of a suitable static electric field. Except for small corrections, the latter frequency is the cyclotron frequency of the proton. The ratio of the two frequencies therefore directly gives the proton magnetic moment in nuclear magnetons. The other method, introduced by Bloch & Jeffries (11), is quite similar except that in this case the proton orbit is shrunk, instead of increased, in what is essentially a small cyclotron run backwards. Bloch finds, with no diamagnetic correction, that the proton magnetic moment is $2.79245 \pm .0002$ nuclear magnetons while Sommer, Thomas, & Hipple obtain $2.79268 \pm .00006$ for the same quantity.

An important experiment, which is in many ways similar to the preceding two, is that of Gardner & Purcell (35) in which the precession frequency of the proton magnetic moment is measured in the same magnetic field as that in which the orbital frequency of electrons rather than protons is measured.

[1] This review is essentially a survey of papers published in 1950.

This experiment therefore directly leads to the proton magnetic moment in Bohr magnetons which is found to be $(1.52100 \pm .00002) \times 10^{-3}$ Bohr magnetons. The ratio of the preceding results to this result directly gives the ratio of the mass of the proton to that of the electron.

Also closely associated with the preceding experiments are the measurements of Thomas, Driscoll & Hipple (108) in which the proton precession frequency is measured in a magnetic field that is carefully calibrated in absolute units. This result then directly leads to the gyromagnetic ratio of the proton magnetic moment which is found to be $\gamma_p = (2.67528 \pm .00006)$ sec.$^{-1}$ gauss^{-1}. If this result is combined with that of Gardner & Purcell (35) the combination provides a precision determination of e/mc.

In 1950 two new methods of nuclear moment measurements were introduced by Hahn (44, 45). The first of these (44) is a relatively minor modification of the normal procedure and is appropriately called nuclear induction by free Larmor precession since the induced signal is received only after the oscillatory field is turned off so that the nuclei are freely precessing in the external magnetic field and consequently inducing an oscillatory magnetic field in the receiving loop as they precess. The other method (45), called the spin echo method, appears to have quite important applications both in studying relaxation phenomena and in precision measurements. In this method a resonant oscillatory pulse is applied for a short time and then removed. Signals from the previous free larmor precession are observed for a short time, but these rapidly disappear in a time of the order of the transverse relaxation time T_2. At a time τ later where $T_2 \ll \tau \ll T_1$, a second resonant radiofrequency pulse is applied and then removed. It is then found that at a time τ after the application of the second pulse a radiofrequency pulse is induced in the receiving circuit. This signal, which apparently arises spontaneously at a time 2τ after the initial pulse is applied, is called a spin echo. The origin of this spin echo can most easily be understood by considering the special case in which the first applied pulse is of just sufficient magnitude and duration to move the resultant magnetization from being parallel to the external magnetic field by a 90° angle so that it becomes perpendicular to same. After a further time T_2, however, because of transverse relaxation phenomena or perhaps field inhomogeneities, the nuclear moments which were originally pointing in one direction in a plane perpendicular to the external field will be pointing in all directions in that plane. However, for lengths of time short compared to T_1, they will still remain in that plane. If, at the time τ after the first pulse, a second pulse is applied whose magnitude (to simplify the discussion) is just double that of the original pulse, then this entire plane will be rotated 180° (twice the original 90°). The nuclear moments will therefore tend to unwind their loss of phase resulting from the transverse relaxation phenomenon and will exactly unwind after a time τ, i.e., after the time in which they originally got out of phase. The method is somewhat analogous to having a number of runners all of whom run at different but constant speeds. If they were started in one direction they would

soon be spread out because of their different speeds. However, if, at a time τ after the start, each runner simultaneously reversed his direction, one would find that, at a time 2τ after the start, all were neatly drawn up abreast at the starting line.

A new method of measuring nuclear moments by the molecular beam magnetic resonance method was introduced by Ramsey (92). This method for many experiments makes possible increases in the precision of the measurements by factors of 10 to 100. In this method the oscillatory magnetic field is introduced only at the beginning and at the end of the homogeneous magnetic field. The resonance frequency then depends only upon the average value of the homogeneous magnetic field and not upon its value at every point. The resonances are therefore not broadened by field nonuniformities; such broadening has been the limiting factor in many earlier molecular beam resonance experiments. This method was successfully applied to hydrogen and deuterium by Kolsky, Phipps, Ramsey & Silsbee (57).

Pound (20, 76) for the first time extended the nuclear magnetic resonance absorption method to the measurement of nuclear electrical quadrupole moment interactions in crystals. The torques exerted by the crystalline electric fields give rise to changes in the nuclear precession frequencies and from observations of these shifts the spins and quadrupole interactions can be inferred. Also he finds he can infer some quadrupole interaction data from relaxation time measurements in certain crystals. These methods prove to be valuable not only as a means of learning nuclear spin and quadrupole moment information but also as a means of studying crystalline structure.

Kastler (50, 96) and Bitter (9) have introduced optical means of observation of the occurrence of nuclear magnetic resonances by the changes in the intensity and polarization of light emitted by atoms in a magnetic field having an oscillatory component.

Ramsey & Pound (95) have introduced a new resonance method called nuclear audiofrequency spectroscopy by resonant heating of the nuclear spin system. This has been successfully applied to LiF which has such a long relaxation time T_1 that, after the crystal is first placed in a strong magnetic field, it takes about 5 min. for the nuclei to become aligned, as can be measured by the strength of the Li resonance. If the crystal is removed from the field for a time short compared to 15 sec., however, the alignment can be immediately recovered when the crystal is reinserted in the strong field. It is found, however, that this property is destroyed if the sample is exposed to a suitable oscillatory magnetic field at about 60 kc. while away from the strong field. The spectrum for destroying this property can be observed and measures the spin-spin interactions within the crystal lattice.

New Phenomena Associated with Nuclear Moment Measurements

Some of the most important discoveries reported in 1950 related to the newly found dependence of the apparent magnetic moment of the nucleus upon the substance in which it was measured. These discoveries were of

great importance both in that they indicated a fundamental limitation to the precision of nuclear moment measurements and that they provided a new means of exploring solid state and molecular properties.

The first such shift was reported by Knight (53) in metals. This was then explained by Townes, Herring & Knight (112) and by Kohn & Bloembergen (55) as due to the paramagnetism of the conduction electrons in the metal.

The next shift in resonance frequency was independently reported by Knight (53), Dickinson (28), and Proctor & Yu (82, 84). This was a shift observed when the nuclear resonance was in different molecular compounds. The theory of this shift was developed by Ramsey (93) and less extensively by Proctor & Yu (82). They attributed the shift to the difference in the magnetic shielding of the nucleus by the electrons of the molecule. Ramsey (93) showed, in particular, that the magnetic shielding in a molecule consists of two parts, of which one is similar to that for an atom while the other corresponds to second-order paramagnetism. Both of these terms can vary from molecule to molecule and one of them, the second-order paramagnetism, can sometimes be quite large. Although Ramsey's expression for the magnetic shielding is generally applicable to all molecules, enough molecular data are usually not available to obtain theoretically numerical calculations of the shielding constant for the molecule. However, for the important case of H_2, the necessary molecular data are available from the molecular beam experiments of Kolsky, Phipps, Ramsey & Silsbee (57) so that the shielding constant can be determined (64, 71, 93, 107). Since there is no correction for the neutron and since the correction can be calculated for atomic helium, the shielding can be evaluated for the lightest nuclei whence ratios of magnetic moments with these nuclei can have more direct nuclear meaning than in the case of the more complicated nuclei.

Dickinson (12) also observed a dependence of the resonance frequency upon the concentration of paramagnetic ions in the solution used even with spherical samples. Bloembergen & Dickinson (12) successfully attributed this to the dependence of the effective g value of the paramagnetic ion upon the angle between the external magnetic field and the electric field of any nearby ion of the nucleus being studied. This dependence will prevent the magnetic field from the paramagnetic ion from averaging to zero at the nucleus being studied even with a spherical sample.

It was found by Ochs, Logan & Kusch (73) that the ratio of the nuclear moments of K^{39} and K^{41} was different from that of their hyperfine structure constants by about 0.2 per cent, which is analogous to an earlier discovery of a similar hyperfine structure anomaly with the rubidium isotopes. Both of these anomalies could be successfully explained qualitatively by suggestions made by Bitter (8) and by Kopfermann (57a) and developed by Bohr & Weisskopf (14). They attribute the hyperfine structure anomaly to a markedly different distribution of the nuclear magnetism throughout the volumes of the nuclei in the two cases. For this reason, then, the hyperfine structures are not simply proportional to the magnetic moments. This interpretation

opens the possibility of exploring the distribution of the nuclear magnetism in the nucleus.

Proctor & Yu (84) have found a similar anomaly between the ratio of the magnetic moments of Cl^{35}/Cl^{37} and the hyperfine structure of the two isotopes. It appears to be much more difficult to explain away the anomaly in this case by the theory in the preceding paragraph because the electronic states in this case are $P_{3/2}$ states whence the electron density at the nucleus is much less as a result of which the dependence of the hyperfine structure interaction upon the distribution of the nuclear magnetism should be much less. Recent experiments of Jaccarino & King (49), however, indicate that the anomaly in the case of the Cl isotopes may be due merely to experimental errors in the earlier measurements of the Cl hyperfine structure.

Another nuclear moment anomaly developed and was explained away. In the atomic molecular beam experiments (61), it is possible to observe not only hyperfine structure but in certain cases the direct interaction of the nuclear moment with the external magnetic field. In this case the measured values of the nuclear moments should agree with those by resonance experiments in mollecules. Nevertheless, for both gallium (61) and indium (84), discrepancies of the order of 0.7 per cent were observed. This was finally explained by Foley (33) as being due to the mixing of the $^2P_{1/2}$ and $^2P_{3/2}$ states of the atom by the external magnetic field in such a way as to account for the discrepancy in the atomic measurements.

A still different anomaly was observed in ratio measurements with the nuclear quadrupole moment interactions. Dehmelt & Kruger (26, 27, 36) found that the ratio of the nuclear quadrupole moments of Cl^{35} to Cl^{37} varied in different molecular compounds. Most of the proposals for accounting for this anomaly have proved to be unsatisfactory. However, a proposal of Gunther-Mohr, Geschwind & Townes (40) that the anomaly is due to the polarizability of the nucleus may prove to be satisfactory.

Pound, Purcell & Ramsey (77, 87, 95) performed a series of experiments with LiF crystals which have a very long relaxation time. They find, among other things, that the spin system is essentially isolated for times which vary from 15 sec. to 5 min. and that, for times short compared to these, the spin system can be placed in a state of negative temperature. In a negative temperature state the high energy levels are occupied more fully than the low, and the system has the characteristic that, when radiation is applied to it, stimulated emission exceeds absorption.

Nuclear Moment Measurements

Many new measurements of nuclear moments were reported in 1950. Among the most important measurements were those described in the section of this report on new methods in which values were listed for the proton magnetic moment in nuclear magnetons, Bohr magnetons, and absolute units. These experimental results were of fundamental importance in that they fixed the scale for all other nuclear moment measurements as well as

providing the most accurate measurements for some of the fundamental constants.

New measurements of the deuteron quadrupole moment interaction energy were completed with a new molecular beam magnetic resonance method by Kolsky, Phipps, Ramsey & Silsbee (56), and new calculations of the gradient of the electric field were made by Newell (70). The combination of these two results gives for the electrical quadrupole moment of the deuteron $(2.738 \pm .016) \times 10^{-27}$ cm.^{2}.

Elements for which there are new data (66) as to the spin, the magnetic dipole moment, the electric quadrupole moment, the hyperfine structure interaction, or the isotope shift are n (46, 88), H (11, 35, 57, 85, 103, 108), D (56, 63, 64, 70, 85, 101), B (38, 115), C (19), N (7, 81, 84, 98), F (41), Na(41), Al (41), S (31), Cl (27, 36, 81, 84, 102), K (23), Sc (48, 83, 84, 94, 100), Mn (4, 30, 81, 84), Co (81, 84), Cu (4, 81, 84), Zn (24), Sc (6, 37), Y(58), Nb (99), Lc (52), Rh (59), Ag (25), Cd (80, 84), In (17, 67, 68), Sn (80, 84), Sb (22), Te (34), I (26), Xe (54, 83, 84), Ba (3), Nd (10), Pr (21), W (34), Tl (80, 84), Pb (69, 80, 84), Bi (51, 83, 84), U (106).

Theoretical Interpretations

Some of the most important results of theoretical studies in 1950 have already been given in the section of this report on new phenomena. This, for example, is true of the theories of magnetic shielding of nuclei in molecules, of the theories explaining the various hyperfine structure anomalies, and of the quadrupole moment interaction anomalies. These theories will therefore not be presented again in the present section.

One of the most significant theoretical developments in nuclear electrical quadrupole moment measurements was that of Sternheimer (105), who showed that the inner electron shells of an atom partly shield the nucleus from the gradient of the electric field from the outer charged particles. Consequently, gradients calculated from the latter alone are likely to be in error by approximately 4 to 45 per cent, leading to errors in the measured quadrupole moments of this amount. Sternheimer's correction, however, does not apply to the quadrupole moment of the deuteron since in this case the effects of all the electrons are included in the calculation. However, the measurements of all other nuclear quadrupole moments have an uncertainty resulting from this phenomenon.

Breit & Arfken (15, 16) suggested a new interpretation of at least part of the isotope shift of atomic spectra. They suggest that this may be due to the polarization of the nucleus by the atomic electrons and due to different isotopic nuclei having different polarizabilities. They point out that this hypothesis can account for the observed odd-even staggering of the isotopic shifts since odd isotopes of even elements should have greater polarizability.

The theories of the origins of nuclear magnetic moments were extended during 1950. Most of these were based on the various shell models of the nucleus (32, 89, 111, 113, 114). Considerable difficulty was experienced (5,

79, 111) in accounting for the sign of the quadrupole moment of Li^7 which was found by Kusch (60) to be positive, despite predictions of the simplest shell models to the contrary. To account for the large magnitudes of many nuclear quadrupole moments, Rainwater (90), Bohr (13), and Preiswerk (78) considered nuclear shell models in which the nucleons moved in fields which were not spherically symmetrical. Further considerations were also given to exchange contributions to nuclear moments (104).

The original theory of Bohr on the effects of internal nuclear motions on the hyperfine structure of deuterium was further developed by Low (65).

There were numerous advances in the interpretation of nuclear resonance phenomena. Some of these have already been described in earlier pages of this report. Others included further developments in the theory of nuclear hyperfine structure of paramagnetic resonance spectra in crystals (1, 86), the theory of magnetic resonance line shapes (2, 97), the theory of the electrical molecular beam method (47), and Hartree calculations of the internal diamagnetic field in atoms (29).

New procedures were developed for studying molecular structure by nuclear moment observations. Townes (110), Gordy (38), and their associates developed means for studying molecular structure with microwave spectra, while Gutowsky & Pake (43) and Newman (72) used the resonance frequencies, line shapes, and relaxation times of the nuclear magnetic resonance method. Ramsey (91) showed that the quadrupole moment of the electron distribution in molecular hydrogen could be obtained from molecular beam magnetic resonance studies.

Purcell & Ramsey (88) reviewed the theoretical arguments indicating that the neutron should have no electrical dipole moment and pointed out that the parity assumptions on which they are based need not necessarily apply to nucleons for which there is as yet no suitable theory. They proposed an experiment for either detecting or setting a very low upper limit to the magnitude of the neutron electrical dipole moment.

Further developments occurred in the means of determining nuclear spins of excited nuclear states from nuclear reaction studies, and from angular correlations of the particles and quanta emitted by the excited nucleons (74), and are described in other sections of these reviews.

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THE NUCLEAR INTERACTIONS OF COSMIC RAYS[1]

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Introduction

A large proportion of recent cosmic-ray research has been devoted to studies of a group of interrelated phenomena which are broadly classed as "nuclear interactions." These are not explained by the modern theories of quantum electrodynamics, which have so successfully interpreted ionization by collision, the Compton effect, the photoelectric effect, and electron-photon cascade showers. The nuclear interactions are of a different type, requiring forces of a nature other than electromagnetic. These forces are intimately connected with the nature of the atomic nucleus. The energies of the cosmic rays which produce these interactions overlap and transcend by a factor of more than 10,000 the particle energies of a few hundred million electron volts which are produced in the laboratory by artificial means. These tremendous energies result in new and interesting nuclear processes, which must be interpreted by an adequate theory of nuclear forces.

Several powerful research tools, alone or in conjunction with one another, continue to be used in cosmic-ray studies. Ionization chambers, proportional counters, Geiger-Mueller counters, Wilson cloud chambers, nuclear research emulsions, and scintillation counters are used as detectors of charged particles. In particular, electron-sensitive nuclear research emulsions are yielding highly important data. The exploitation of scintillation counters is in early stages.

The nomenclature for the various nuclear interactions stems directly from the techniques which have been used to study them: the "penetrating showers" which have been observed in Geiger counter coincidence experiments and in cloud chambers, "stars" and "nuclear disintegrations" which have been observed in nuclear research emulsions and in cloud chambers, and "bursts" which have been observed in ionization chambers. Some of these terms describe similar or related events.

The term "penetrating shower" is applied to a group of two or more simultaneously detected "penetrating particles." A "penetrating particle" is one which is capable of traversing a certain minimum thickness of absorbing material without interaction. This minimum thickness varies between 10 and 50 cm. of lead in Geiger counter experiments, thus assuring that a penetrating particle is not an electron. Penetrating showers are usually produced in the dense material in and above the detecting apparatus. They are the result of high energy nuclear disintegrations.

The term "star" defines an event in which two or more heavily ionizing particles are observed to originate in a common point in a nuclear research

[1] This review is essentially a survey of papers published in 1950.

emulsion or in plates or foils placed in a cloud chamber. The tracks of the particles are referred to as "prongs." Such events are usually produced by particles which have less than 200 M.e.v. kinetic energy. The term "nuclear disintegration" is used to describe events in which one or more lightly ionizing particles, in addition to heavily ionizing particles, originate in a point. Such an event is sometimes referred to as a high energy star. Conversely, a star (of low energy) is sometimes called a low energy nuclear disintegration. Sufficient evidence is now available to identify penetrating showers with the high energy nuclear disintegrations which are seen in nuclear research emulsions and in cloud chambers.

The experiments which are described below have been designed (*a*) to study the particles which initiate the nuclear interactions—their identification, their mean free path for interaction, their energies, their intensities, and their probable origin—and (*b*) to study the particles which are produced in the interactions—their identification, their mean free path for further nuclear interactions of the same or different types, their multiplicity of production, and other factors bearing on the nature of the nuclear event. It will be convenient to refer to the initiating particles as "primary particles" or, simply, "primaries." The particles produced in the interactions will be referred to as "secondary particles" or, simply, "secondaries." Both the primaries and those secondaries which are capable of further nuclear interactions have also been designated "N-rays" by Rossi (1).

A brief, simplified account of cosmic-ray nuclear disintegrations follows. The highest energy events occur at the top of the atmosphere and are produced largely by the protons, alpha particles, and heavier nuclear fragments which are isotropically incident upon the earth's atmosphere from outer space. Less energetic events are produced deeper in the atmosphere by neutrons, protons, alpha particles, π-mesons, and possibly yet unknown particles.

When a high energy proton strikes a nucleus it collides sharply with one of the nucleons. As a result of this nucleon-nucleon collision, a number of relativistic π-mesons, charged and neutral, are created. Because of the creation of matter at the expense of some of the kinetic energy of the incident particle, the collision is said to be inelastic. The mesons spray out of the nucleus in a narrow cone, traveling roughly in the same direction as the incident particle, and thus conserving the momentum of the incident particle. Relativistic nucleons may also accompany the mesons. In addition to the inelastic collision there frequently occur in the same event less violent elastic collisions, which transfer relatively smaller amounts of energy to some of the remaining nucleons. These successively collide with other nucleons, producing a general "heating" of the residual nucleus, which then "evaporates" nonrelativistic nucleons isotropically until it "cools" to a stable state or is completely disintegrated. Thus, in addition to π-mesons, there are also produced protons, neutrons, alpha particles, and sometimes larger fragments of the original nucleus. There is strong indication, at least in the case of high

energy disintegrations of the heavier nuclei, that more than one inelastic nucleon-nucleon collision can occur inside a single nucleus.

Each neutral π-meson produced in these interactions decays almost at once into two high energy photons, which in turn give rise to the electron-photon cascade showers, the soft component of cosmic radiation. The charged π-mesons also decay quickly, yielding μ-mesons, which are sufficiently long-lived for most of them to penetrate to sea level. A few of the μ-mesons decay in flight into electrons which contribute to the soft component.

There is some experimental evidence indicating that V-particles and τ-mesons—if indeed the latter exist—also originate in these violent collisions.

The Charge of the Primary Particles

Statistical data show that almost all of the nuclear disintegrations occurring near the top of the atmosphere are produced by charged particles. These are the protons, alpha particles, and heavier nuclear fragments which come from outer space. Deeper in the atmosphere, at mountain elevations, the disintegrations are produced about equally by charged and neutral particles, the neutral particles predominating at low energies and the charged particles predominating at very high energies.

Near the top of the atmosphere, statistical data on this point have been derived principally from nuclear research emulsions. In meson-producing interactions the mesons spray out in a more or less narrow cone, conserving the momentum of the primary particle. The direction of the mesons thus defines the direction of the primary particle, which will then be visible if it is charged, and not visible if it is neutral. For most of these disintegrations, a charged primary particle is observed. For example, Lord & Schein (2), in an analysis of about 500 disintegrations recorded at 29,000 m. (14 gm./cm.^{2} residual atmosphere), found no definite case in which a well-defined cone of relativistic particles was not accompanied by a charged incident particle. An exception to this was found by Leprince-Ringuet, Bousser, Hoang-Tchang-Fong, Jauneau & Morellet (3), who observed one high energy disintegration which showed no incident charged particle. This event, which was obtained in a nuclear research emulsion exposed at 30,000 m. altitude, showed 27 non-relativistic particles plus a group of 27 collimated relativistic particles. The production of nuclear interactions almost exclusively by charged particles at the top of the atmosphere is consistent with the concept that the incoming particles are all charged. The single high energy event, observed by Leprince-Ringuet, *et al.*, can be interpreted as production by a very high energy secondary particle, possibly a neutron.

Observations show that nuclear disintegrations produced at mountain elevations are produced with about the same frequency by neutral as by charged particles. Using Geiger counters Walker, Walker & Greisen (4) found a ratio of neutral to charged particles (N/C) of 0.84 ± 0.13 at an elevation of 4,260 m. (Mt. Evans, Colorado). In this experiment the nuclear interactions

were produced in a 4-in. layer of lead. Only those events were counted which produced at least two particles capable of penetrating an additional 4 in. of lead absorber. Geiger counters placed above the producing layer were used to determine the relative numbers of neutral and charged primaries. A raw data value of $N/C = 0.28 \pm 0.03$ was corrected for back-projected particles from neutral-particle-induced events, which would simulate charged-particle-induced events, and back-projected particles from charged-particle-induced events striking the same counter as the charged primary particle, events of a type that would not be counted in neutral-particle-induced events.

At 3,260 m. elevation (Echo Lake, Colorado) Cocconi, Cocconi Tongiorgi & Widghoff (5) found a ratio N/C also of the order of unity. The experiments employed Geiger counters in coincidence with neutron-sensitive proportional counters. The events counted were interactions involving the production, in a $4\frac{1}{2}$-in. lead producing layer, of at least one charged particle capable of crossing 22 gm./cm.^{2} of paraffin in addition to the lead remaining below the point of the interaction, and accompanied by two or more neutrons having energies in the range 1 to 15 M.e.v. The data were corrected for particles projected backward from the disintegration.

That most of the very high energy interactions ($\sim 10^{10}$ e.v.) at 3,500 m. elevation (Climax, Colorado) are produced by charged particles is suggested by recent cloud chamber experiments of Gottlieb, Hartzler & Schein (6). Sixteen 1-cm.-thick gold plates were placed across the chamber, which was triggered whenever a nuclear event produced at least three penetrating particles capable of crossing 10 cm. of lead below the chamber in addition to the gold plates below the point of the interaction. The topmost counter of the triggering arrangement was placed in the center of the chamber so that events occurring in the upper half of the chamber could be initiated by either neutral or charged particles. Analysis of 73 events showed that 81 per cent were produced by charged particles and only 4 per cent by neutral particles, the remaining cases being questionable. The statistical weight of these findings is low; however, if the result is real it may indicate that these events are produced by the primary cosmic radiation, a small fraction of which may survive to great depths in the atmosphere. In support of this argument Gottlieb *et al.*, extrapolate from the frequency of their observed events, using a geometrical cross section for air nuclei (67 gm./cm.^{2}), to predict a vertical primary radiation flux of 0.029/cm.^{2} sec. steradian. This compares favorably with a flux of 0.02/cm.^{2} sec. steradian for particles of energies above 10^{10} e.v., which was calculated from the value 0.10/cm.^{2} sec. steradian for the primary flux at 55° N. geomagnetic latitude (7). A power law spectrum was used to give the flux for high energy particles alone.

Although the very high energy disintegrations may correspond to that small fraction of the primary cosmic radiation which survives to mountain elevations, the lower energy events which are produced almost equally frequently by charged and by neutral particles can be looked upon as produced predominantly by secondary particles, themselves the result of higher energy nuclear interactions or other processes taking place higher in the atmosphere.

The Mean Free Path for Nuclear Interaction

A number of investigators in recent years have attempted to measure collision mean free paths for particles capable of producing nuclear interactions. A comparative evaluation of their results is difficult, partly because it is not clear in some experiments—even when well planned—exactly what has been measured, and partly because apparently comparable data actually refer to different things, which should therefore not be compared. Nearly all investigators compare their results with calculated mean free path values which are based upon geometric cross sections of nuclei, under the not unreasonable assumption that these should be the limiting values for high energy interactions. As will be pointed out below, this assumption is partly

TABLE I

Collision Mean Free Paths for Nuclear Interaction*

Absorber	Mean Mass Number, A	Mean Free Path, λ
Carbon	12	61 gm./cm.^{2}
Air	14.5	65
Aluminum	27	81
Iron	56	103
Lead	207	160

* Based on the average nuclear radius, $r = 1.4\ A^{1/3} \times 10^{-13}$ cm.

verified by experiment, but there remain several apparently contradictory results.

There are several published formulas for the average geometric cross sections of the elements. These are based upon the following average nuclear radii: $1.4\ A^{1/3} \times 10^{-13}$ cm. [Rossi (1)], $(0.5 + 1.37\ A^{1/3}) \times 10^{-13}$ cm. [Greisen (4)], and $1.5\ A^{1/3} \times 10^{-13}$ cm. [Bethe (8)]. Values given by these do not differ much from each other, except perhaps for the fact that Greisen's formula gives somewhat smaller cross sections for the lighter elements. Table I lists geometric mean free paths computed from Rossi's formula, which yields $\lambda = 27\ A^{1/3}$ gm./cm.^{2}.

The average distance traveled by a group of particles before they produce a nuclear interaction, i.e., their mean free path, depends upon the nature and energies of the particles as well as upon the nature of the struck nucleus. The ambiguities which arise in the interpretation of the experimental mean free path values are usually directly related to ambiguities in the identification of the particles studied, and in the determination of their energies. These in turn arise through the use of imperfect, but nevertheless useful, research techniques. For convenience, the experimental methods will be classified as (*a*) direct measurements, (*b*) comparative measurements, and (*c*) absorption measurements. Each of these will be defined as the experimental data are discussed.

Direct measurement of mean free path.—In cloud chamber photographs and in nuclear research emulsions the tracks of charged particles are visible, and so a direct application of the mean free path definition is possible. The path length of each of the particles under consideration is measured and the number of nuclear interactions that they produce is counted. The sum of the path lengths divided by the number of interactions then gives the collision mean free path. In principle, the method should give accurate results. However, it is not always possible to exclude from the path length determination

TABLE II

CLOUD CHAMBER DATA. MEAN FREE PATHS FOR NUCLEAR INTERACTION OF PARTICLES WHICH ARE SECONDARY TO NUCLEAR INTERACTIONS

Investigator	Elevation	Mean Free Path		Energy of Secondaries
		(gm./cm.^{2})	Relative to Geometric MFP	
Fretter	3,027 m.	750, Pb	4.7	>400 M.e.v.
Lovati, Mura, Salvini, and Tagliaferri	3,500 m.	300 ± 90, Pb*	1.9	>150 M.e.v.
Brown and McKay	3,260 m.	316 ± 70, Pb*	2.0	>150 M.e.v.
Butler, Rosser, and Barker	sea level	200, Pb*	1.3	Average energy of shower $\backsim$7 B.e.v.
Green	2,700 m.	237 ± 29, C	3.9	—

* Value corrected for inefficiency in detection of low energy stars.

extraneous particles such as electrons and μ-mesons; further, the efficiency for detection of nuclear disintegrations, particularly at low interaction energies, may be low. These factors must be considered in an interpretation of the data.

Except for the heavier nuclear fragments which are encountered at the top of the atmosphere, the collision mean free path data obtained in this manner concern particles which are directly observed to arise themselves in nuclear interactions. Table II lists values for carbon and lead nuclei, which were measured in cloud chambers. All of these values are in excess of the geometric mean free paths; values for lead range from 1.4 to 2.0 times the geometric value, and the one value reported for carbon is about four times the geometric value. Measurements in nuclear research emulsions, which may have a significant bearing on the carbon data, will be discussed first.

Camerini, Fowler, Lock, & Muirhead (9) reported data on the mean free path in nuclear research emulsions for the production of nuclear disintegrations by particles which are observed to originate in other nuclear disintegrations in the emulsion. Ilford G5 emulsions were exposed by means of balloons at an altitude corresponding to 50 gm./cm.^{2} residual atmosphere. The results of these experiments are particularly interesting because an identification of those particles which are π-mesons was made, through the use of multiple scattering measurements. The collision mean free path for 241 π-mesons, which produced a total of six nuclear disintegrations, is (82 ± 35) gm./cm.^{2}. This value is in good agreement with the average geometric mean free path for this emulsion, which is 90 gm./cm.^{2}. The mean free path for all of the secondary particles, including π-mesons, is (102 ± 25) gm./cm.^{2}. This value indicates that the cross section for π-mesons in this second measurement is also roughly geometric, because the cross section for protons, which are most likely the remaining constituent of this sampling of particles, is roughly geometric for the energy range 100 to 600 M.e.v.

Camerini *et al.*, note in particular that the types of stars produced are of very low energy and therefore suggest that the corrections which have been applied to cloud chamber data may be too small. (See discussion below.)

Lovati, Mura, Salvini & Tagliaferri (10) measured the collision mean free path in lead for particles which are secondary to other nuclear disintegrations. They used a cloud chamber containing lead plates of two thicknesses, 1.8 and 16.5 gm./cm.^{2}. The relative number of nuclear events observed in the thick and the thin plates served as a measure of the efficiency for detection of the events. The absolute efficiency for thin plates was taken from the data of Bridge, Hazen, Rossi & Williams (11). The criterion used for the selection of nuclear disintegrations are (*a*) the production of at least two particles, at least one of them being heavily ionizing, (*b*) the production of at least four relativistic particles in a thin plate, or (*c*) the production of two penetrating particles in the first of the two thick plates used. Large angle scatterings ($>10°$), which comprise 7 of the 36 nuclear events reported, were included in the mean free path calculation. The measured value, corrected for the efficiency for detection of the events, is (300 ± 100) gm./cm.^{2}. This is approximately twice the geometric mean free path.

Brown & McKay (12) made similar measurements using five lead plates, each 14.5 gm./cm.^{2}, in their chamber and somewhat different criteria for selection of nuclear events. Their minimum requirements for a nuclear event are the emission of (*a*) one penetrating particle and one heavily ionizing particle, (*b*) one heavily ionizing particle and one lightly ionizing particle, or (*c*) two heavily ionizing particles. They defined a penetrating particle as a lightly ionizing particle capable of penetrating at least one lead plate without cascade multiplication. Large angle scatterings were not included in this measurement. The experimental value, corrected for the efficiency for detection of the nuclear events, is 316 ± 70 gm./cm.^{2}, which again is about twice the geometric mean free path for lead.

Using a cloud chamber previously operated at sea level by Fretter, (13) Green (14) measured mean free paths using 10 1-in. carbon plates with four $\frac{1}{2}$-in. lead plates placed below them in the chamber. A Geiger-tube selection of events which were photographed required that at least one counter above, and at least two counters below the chamber be actuated. Thus, for nuclear events occurring in the carbon to be photographed, at least two particles capable of penetrating 4 in. of lead had to be produced. (An additional 2 in. of lead was placed between the chamber and the bottom counters.) Penetrating showers and stars were the nuclear events which were considered in the computation of the mean free path. A "penetrating shower" was defined as an event involving the emission of (*a*) two or more penetrating particles, (*b*) one or more heavily ionizing particles, (*c*) one penetrating and three nonpenetrating particles, or (*d*) one nonpenetrating particle and one penetrating particle making an angle of at least 5° with the primary particle direction. A "star" was defined as an event showing (*a*) at least one nonpenetrating particle and at least one heavily ionizing particle, (*b*) at least two heavily ionizing particles, (*c*) at least four nonpenetrating particles, or (*d*) three nonpenetrating particles provided that at least one of these produced a secondary event. A "penetrating particle" was defined as one which penetrated at least one lead plate without cascade multiplication. A "nonpenetrating particle" was defined as one which penetrated no lead plates, including those particles which failed to reach the lead plates for any reason. Sixty secondary penetrating showers and 29 secondary stars, a total of 89 nuclear events were produced by 677 penetrating and 797 nonpenetrating particles, all of these being relativistic particles. These data yield a mean free path of 237 ± 29 gm./cm.^{2} for the production of nuclear events in carbon by relativistic particles emitted in primary nuclear events in carbon. This value is about four times the geometric value.

Green concluded, tentatively, that his value is large because of a probable inefficiency for detection of very low energy stars which are produced by π-mesons. If the mean free path is indeed geometric, it follows that only one-fourth of the secondary particles counted are capable of producing nuclear interactions which are visible in the chamber; the remaining three-fourths of the particles may be π-mesons, whose low energy interactions are not detected in the cloud chamber. This interpretation finds further support in the previously-mentioned data of Camerini, *et al.* (9), who found that (79 ± 6) per cent of the secondary fast particles produced in nuclear research emulsions are π-mesons. It is possible that a similar argument may explain the high values obtained in cloud chamber experiments for lead.

Comparative measurements of the mean free paths.—In one type of comparative measurement, the production of penetrating showers in various materials is studied with the same apparatus at the same location. A Geiger tube array is arranged to detect penetrating showers which are produced only in a particular layer of material, called the producing layer. In the experiment, precautions must be taken to insure that the events which are

counted are indeed penetrating showers that are produced in the producing layer, and to insure that the substitution of different materials in the producing layer neither changes the geometric arrangement of the apparatus nor changes the energies of the events which are studied. The rates of occurrence of penetrating showers in producing layers of different materials yield relative values of the mean free paths for penetrating shower production by the particles which fall on the apparatus.

A direct comparison of the cross section for production of penetrating showers in lead and carbon was made by Mezzetti & Querzoli (15) at 3,500 m. elevation (Cervinia). An arrangement of Geiger tubes and absorbers was devised to require that the nuclear interactions occur in a definite producing layer and that the interactions each produce at least two particles capable of traversing 7.5 cm. of lead. Table III shows the counting rates for such events

TABLE III

EXPERIMENTAL RESULTS OF MEZZETTI & QUERZOLI*

Producing Layer	$j=2$	3	4	5	6	7
0	21 ± 2	7.5 ± 1.2	3.4 ± 0.8	1.2 ± 0.5	0.6 ± 0.3	0
17 gm./cm.^{2} C	49 ± 3	24.8 ± 2.3	12.9 ± 1.6	6.5 ± 1.3	2.0 ± 0.6	0
47 gm./cm.^{2} Pb	37 ± 3	20.4 ± 2.1	12.1 ± 1.6	7.5 ± 1.3	5.3 ± 1.1	1.9 ± 0.6

* Frequencies in $(100\ \text{hr})^{-1}$ of nuclear interactions involving the production of j particles, at least two of which penetrate 7.5 cm. of lead.

for (*a*) no producing layer, (*b*) 17 gm./cm.^{2} carbon producing layer, and (*c*) 47 gm./cm.^{2} lead producing layer. The values chosen for carbon and lead give equal geometric mean free paths. In the table, the numbers $j=2$ to 7 indicate the numbers of particles coming out of the producing layer and incident on the lead absorbing layer below it. The numbers were determined by a series of Geiger tubes which were placed under the producing layer.

Those coincidences involving only a single particle incident upon the absorbing layer, and of course two particles below the layer, were interpreted as caused by single penetrating particles which produced knock-on secondaries in the lead. (This view is supported by the fact that this counting rate was independent of the presence or absence of the producing layer.) Those coincidences having at least two particles incident on the lead might have been caused by (*a*) penetrating showers generated in the producing layer, (*b*) penetrating showers generated in the counter walls or other material above the producing layer, presumably the result of the inefficiency of the counter telescope above the producing layer to count only single incident particles, (*c*) double knock-on secondaries of single penetrating particles, (*d*) random coincidences, (*e*) cascade showers, (*f*) showers incident laterally on the apparatus which escape elimination by a series of air shower counters,

or (*g*) penetrating showers generated in the absorbing layer and having backward-emitted particles. The possibilities (*b*), (*c*), and (*d*) were either calculated or measured, and corrections to the data for them were made. The effect of cascade showers was investigated and found to be negligible. Possibilities (*e*) and (*g*) were considered to be independent of the presence or absence of the producing layer, and hence measured by the counting rates obtained with no producing layer. The differences in counting rates with no producing layer and with carbon or lead producing layers, corrected for the effects (*b*), (*c*), and (*d*), were taken to be the production rates in the two materials. The final result is a ratio of the collision mean free paths in lead and carbon of 4.4 ± 1.0, a result not incompatible, according to the investigators, with the geometric mean free path ratio of 2.6. This value will be compared below with that of Walker, *et al.*, obtained by a different method.

A different type of direct comparison experiment was carried out by Barbour & Greene (16), who employed thin foils of gold, platinum, nickel, copper, tin, and aluminum sandwiched between nuclear research emulsions and exposed to cosmic radiation at 23,500 m. altitude. Stars produced in the foils were observed by means of their prongs which penetrated to the emulsion layers. For each material, integral cross sections for production of stars of at least ten, at least eight, at least six, and at least four prongs were obtained. When the cross sections are plotted for each group of star sizes as a function of nuclear mass number A, the variation with mass number is consistent with the form $\sigma = kA^s$ with values of $s = 2.0$, 1.5, 1.0, and 0.7 for stars of at least ten, eight, six, and four prongs, respectively. On the basis of an estimated extrapolation, a value of $s = 2/3$ is obtained for stars having at least two or three prongs, in harmony with the expected value, assuming geometric cross sections.

Absorption measurements in dense materials.—Absorption measurements can be expected to lead to an upper limit for the collision mean free path. These measurements are usually carried out for particles which fall on the apparatus from above, in contrast to some of the measurements discussed above which concerned particles secondary to interactions which occur in the apparatus. For absorption measurements in dense materials, any of the several detectors of nuclear interactions can be used to measure the rates at which interactions occur when various thicknesses of absorber are placed over the detector. An "absorption mean free path" can be defined as the absorber thickness which decreases the interaction rate to $1/e$ times some initial value. If the absorption is exponential, the absorption mean free path will be constant with increasing absorber thickness.

A complete series of absorption measurements for dense materials is usually made at one location. The same is also true for absorption measurements in air provided that variations in barometric pressure are great enough at a given location to produce a significant change in the mass of air over the apparatus.

The absorption mean free path should be identical with the collision

mean free path provided that the interacting particles are lost only by nuclear interactions, and provided that no appreciable number of secondary particles, themselves capable of initiating further interactions in the detector, are produced in the absorber. It is well known that particles resulting from sufficiently high energy nuclear interactions are capable of further interaction, so that one may expect absorption mean free paths to be longer than collision mean free paths. This effect should be more pronounced when the experiments are carried out under conditions which utilize rays of higher average energies.

Several early attempts to measure the collision mean free path by means of absorption measurements resulted in little quantitative information be-

TABLE IV

GEIGER COUNTER DATA. ABSORPTION MEAN FREE PATHS FOR PENETRATING SHOWER PRODUCTION

Investigator	Elevation	Mean Free Path		Penetrating Power of Secondaries
		(gm./cm.²)	Relative to Geometric MFP	
Walker	3,260 m.	147 to 208, Pb	0.9 to 1.3	—
Sitte	3,260 m.	162 ± 10, Pb 196 ± 10, Pb	1.0 1.2	>200 gm./cm.² >100 gm./cm.²
Walker, Walker, and Greisen	4,260 m.	160 ± 10, Pb 81 ± 10, C	1.0 1.3	>115 gm./cm.² >115 gm./cm.²

cause of inherent difficulties in interpretation of the experiments (1). Recent improvements in penetrating shower experiments have resulted in more meaningful data. Experiments reported by Walker (17), Sitte (18), and by Walker, Walker & Greisen (4) yield values which are comparable to the geometric mean free paths for lead and carbon absorbers (cf. Table IV). In this type of experiment the absorption of rays falling on the apparatus is measured. The penetrating shower detector is a set of Geiger tubes imbedded in a large quantity of lead. Suitably defined coincidences of these Geiger tubes detect the production of penetrating showers; specifically, the simultaneous passage of two or more particles which are capable of crossing large amounts of lead is detected. A tray of Geiger tubes, completely covering the penetrating shower detector, is used to select those penetrating showers which are produced in the detector by an ionizing particle (through the requirement that only one of the Geiger tubes be fired) and those penetrating showers which are produced by a nonionizing particle (through the require-

ment that no Geiger tube in the covering tray be fired). Hodoscope arrangements can be used to record which of the individual counters in the detector and the covering tray fired. Through such records it is possible to eliminate spurious events.

Walker's data (17) on the absorption mean free path for nuclear interacting rays at 3,260 m. elevation (Echo Lake, Colorado) show an apparent decrease in mean free path with increasing interaction energies; he assumed that the number of penetrating particles produced in an interaction is a measure of the energy of the interacting particle. His mean free path data range progressively from 208 gm./cm.^{2} of lead for interactions resulting in three shower particles to (147 ± 10) gm./cm.^{2} of lead for interactions producing at least eight shower particles.

Early experiments did not require sufficiently rigid selection of events in so far as the penetrating power of the secondary particles is concerned. Sitte (18) therefore carried out an experiment in which he required that the nuclear disintegrations take place in a suitably defined producing layer so that the secondaries would be required to cross a known minimum thickness of lead. He used hodoscope records to verify that his Geiger counter coincidence criterion assured that the penetrating showers detected actually occurred in the producing layer. Data were obtained for interactions produced by ionizing particles at an elevation of 3,260 m. (Echo Lake, Colorado). Data were taken for lead absorbers of four thicknesses—0, 170, 270, and 350 gm./cm.^{2} placed above the detector. The measurements include two such series, one for secondary particles capable of crossing at least 100 gm./cm.^{2} of lead and one for secondaries capable of crossing at least 200 gm./cm.^{2} of lead. Both absorption curves were found to be exponential within the experimental errors and lead to values for the absorption mean free path which are given in Table IV.

The experiments of Walker, Walker & Greisen (4) measured separately the absorption mean free paths for charged and uncharged particles at 4,260 m. elevation. The experimental arrangement required the production of the penetrating shower to take place in a fixed 4-in. thickness of lead and the penetration of secondary particles through an additional 4 in. of lead placed below the producing layer. A hodoscope arrangement permitted identification of each Geiger counter (there were 85 of them) which fired. Data were taken with a rather loose criterion for penetrating shower detection. In the analysis of the data, the hodoscope records were used to reject each spurious coincidence. The resulting counting rates are given in Table V. The experiments extended to sufficiently great absorber thicknesses to show a clear departure of the absorption curves from exponential form. Walker *et al.*, interpreted this [after Cocconi (19)] as produced by incomplete elimination of background events, which they assumed to be roughly independent of absorber thickness. Background rates were chosen to make the data for lead absorber fall on a least square exponential curve. The constant rate so chosen was applied directly to the data for carbon. The following results were obtained: Neutral primaries in Pb: 164 ± 15 gm./cm.^{2}; charged pri-

maries in Pb: 157 ± 12 gm./cm.^{2}; neutral primaries in C: 80 ± 7 gm./cm.^{2}; charged primaries in C: 82 ± 8 gm./cm.^{2}. These data indicate that the charged and neutral particles have approximately the same cross sections for interaction, a result consistent with the concept that, in the atmosphere at mountain elevations, most of the interacting rays are protons and neutrons, the π-mesons, originally present, having been lost largely by decay into μ-mesons.

Walter *et al.*, interpret their value for carbon as being significantly different from the geometric collision mean free path (61 gm./cm.^{2} on the basis of Rossi's formula, and 48 gm./cm.^{2} on the basis of Greisen's formula) and

TABLE V

DATA OF WALKER, WALKER & GREISEN*

Absorber	Penetrating Showers with Charged Primaries	Penetrating Showers with Neutral Primaries	Total Rate of Discarded Events
Zero	0.723 ± 0.033	0.473 ± 0.017	2.95 ± 0.10
42 gm./cm.^{2} C	0.438 ± 0.022	0.266 ± 0.015	2.76 ± 0.05
71 gm./cm.^{2} C	0.315 ± 0.020	0.212 ± 0.012	2.52 ± 0.06
140 gm./cm.^{2} Pb†	0.286 ± 0.019	0.191 ± 0.013	2.33 ± 0.06
252 gm./cm.^{2} Pb†	0.157 ± 0.014	0.125 ± 0.010	2.26 ± 0.05
364 gm./cm.^{2} Pb†	0.105 ± 0.010	0.075 ± 0.007	2.27 ± 0.05

* Counting rates in (minutes)$^{-1}$ for penetrating showers measured under variou absorbers. Events were discarded, as spurious, by means of hodoscope records.

† Plus 7 gm./cm.^{2} Fe.

therefore indicating a "transparency" of the carbon nucleus to the interacting particles.

Montgomery, Montgomery & Northrup (20) measured the penetrating power of particles associated with stars at 3,510 m. elevation (Climax, Colorado). The stars were detected with a thin-walled ionization chamber. Geiger counters in coincidence with the chambers were used to detect associated particles. The geometric arrangement was such that the associated particles were either produced in the stars, or accompanied the star-producing radiation. The absorption in lead was found to be exponential with an absorption coefficient of 107 ± 30 gm./cm.^{2}, somewhat less than the geometric mean free path. At most, 0.02 per cent of the stars were accompanied by at least two particles capable of penetrating 230 gm./cm.^{2} of lead. If these particles are protons, their mean energy is about 300 M.e.v.; if mesons, about 150 M.e.v. In 1 to 2 per cent of the nuclear events, there were associated electrons, either produced in the stars, or accompanying the star-producing radiation. (A comparison of these data with the above absorption measurements is not made because of differences in the energies of the nuclear events.)

Absorption measurements in air.—Additional absorption coefficients for star and penetrating shower production in air were reported in 1950. The data are of several types, but most seem to confirm the previously reported data; e.g., Tinlot's (1) value of 118 gm./cm.^{2} for the absorption thickness for local penetrating shower production. The "absorption thickness" is defined as the thickness of atmosphere in which the production of nuclear events in the apparatus is changed by the factor $1/e$; this definition has meaning because measurements with a given apparatus at various altitudes usually show an exponential absorption in the atmosphere. The absorption thickness should in general be greater than the absorption mean free path because of the zenith angle distribution of the particles in the atmosphere. The meaning of an absorption coefficient therefore depends upon the geometric arrangement used in its measurement.

McMahon, Rossi & Burditt (21) used a cylindrical ionization chamber, filled with 4 atm. of pure argon and shielded with 15 cm. of lead, to measure the altitude and latitude effects of bursts. Through use of electron collection and records of the shape of the burst pulse, it was possible to determine whether the bursts were caused by showers of relativistic particles or by a few heavily ionizing particles. Five trays of Geiger counters (A) were placed over the lead shield, and one tray of counters (B) was placed just under the ionization chamber (I). The counting rates for triple coincidences of A, I, and B (designated AIB), for double coincidences of A and I in anticoincidence with B (designated AI-B), and for double coincidences of I and B in anticoincidence with A (designated IB-A) were obtained at 55° N. geomagnetic latitude for three altitudes (383, 300, and 273 gm./cm.^{2} residual atmosphere) and at 20° N. geomagnetic latitude for two altitudes (383 and 300 gm./cm.^{2} residual atmosphere). The pulse I of the ionization chamber corresponded to the passage of 60 or more electrons. Of interest in the present discussion are the coincidences AIB. The pulse shape records showed these to be caused by showers of relativistic particles. These showers may be the result of electromagnetic collisions of μ-mesons, of nuclear interactions of high energy nucleons, or of nuclear interactions of π-mesons. Other experiments show that μ-meson events are relatively important only near sea level. π-Meson events should be few because of the large probability for their decay in flight through the atmosphere. McMahon, *et al.*, therefore interpreted a coincidence AIB to be caused by an electron shower started by a high energy photon which was produced in the lower part of the lead shield. To produce the observed showers, the energy of the initiating photon would have to be greater than 5 B.e.v. The absorption thickness for these events was found to be (125 ± 8) gm./cm.^{2} at 55° N. and (135 ± 11) gm./cm.^{2} at 20° N. The two results are not significantly different from each other or from Tinlot's value.

A heavily shielded ionization chamber was used by Stinchcomb (22) to measure the barometric effect for large cosmic-ray bursts at 3,500 m. elevation (Climax, Colorado), corresponding to 675 gm./cm.^{2} residual atmosphere. He used a Carnegie model C ionization chamber shielded with a 12-cm.-thick

spherical lead shield. Data were obtained for bursts corresponding to the passage of 200 or more relativistic particles; 1,145 bursts were recorded in 735.8 hr. at an average pressure of 486.86 mm. Hg, and 1,008 bursts were recorded in 884.0 hr. at an average pressure of 495.26 mm. Hg. After application of a correction for the omnidirectional sensitivity of the apparatus, these data yield a barometric coefficient for the frequencies of bursts produced by the vertical radiation of $-(1.8 \pm 0.5)$ per cent per mm. Hg. This corresponds to a mean absorption coefficient of (74 ± 21) gm./cm.^{2}, a value not inconsistent with the geometric collision mean free path for air.

Frequencies of bursts in thin-walled ionization chambers were measured at very high altitudes by Whyte (23). Except at the top of the atmosphere, such bursts are caused by stars produced in the chamber walls (1). The spherical chambers, 30 cm. in diameter and filled with argon at 1.4 atm., were sent to 23,000 m. in balloon flights made at several geomagnetic latitudes. Electron collection was used. The burst sizes recorded were those greater than one 5.3-M.e.v. polonium alpha particle will produce. At 0° geomagnetic latitude, the number of bursts increased with altitude to the highest altitudes reached. The continued increase near the top of the atmosphere was interpreted as caused directly by the ionization of the heavy nuclei which fall on the earth from outer space. Whyte estimated the flux of these at 0° latitude using the data of Bradt & Peters (24) for the flux at 30° and 51° N. geomagnetic latitude, the approximate energy spectra for the particles as determined by Vallarta (25), and the geomagnetic cutoff energies at 30° and 0°. After correction for the contribution of heavy nuclei, the altitude variation of the bursts shows a broad maximum of intensity at about 7 cm. Hg., corresponding to about 100 gm./cm.^{2} residual atmosphere. Whyte suggests that this maximum is due to nuclear events occurring in cascade in the atmosphere, in loose analogy with the cascade process observed for the soft component near the top of the atmosphere.

The Nature of the Secondary Particles

Studies of the nature and relative numbers of particles produced in nuclear interactions, particularly those of great energy, have been made over a period of years by many investigators. A few of the more recent findings will be discussed here.

Charged particles.—Using Ilford C2 and Kodak NT4 nuclear research emulsions Bernardini, Cortini & Manfredini (26) made a study of star production at 3,500 m. elevation (Cervinia). The frequency of occurrence of various-sized stars, as indicated by the number of observable prongs, was obtained for 5,270 stars in C2 plates and 1,870 stars in NT4 plates. The data were compared with those of Gardner & Peterson (27) who reported information on 781 stars produced by 135-M.e.v. deuterons from the Berkeley cyclotron. The latter data show a negligible number of stars having more than five prongs, whereas 20 per cent of the cosmic-ray stars have more than this number. The size distribution for small cosmic-ray stars is similar to that for

the Berkeley stars, giving support to the suggestion that these cosmic-ray stars are produced by nucleons having energies of the order of 100 to 200 M.e.v. Because protons in this energy range are quickly stopped by ionization loss, neutrons must be the principal small star producers. The lack of many-pronged stars among the Berkeley data can be interpreted as an indication that the cosmic-ray stars with more than five prongs represent interactions of greater energy than the Berkeley stars.

Camerini, Fowler, Lock & Muirhead (9) made an extensive study of the charged particles produced in high energy interactions. Their data were obtained with 400-μ Ilford G5 nuclear research emulsions which were exposed by means of balloon flights at an altitude corresponding to 50 gm./cm.^{2} residual atmosphere. Mass measurements were made on the tracks of 700 particles produced in nuclear interactions. Mass values were computed on the basis of grain counts and measurements of mean scattering angles (28). Grain counting yields a measure of the particle velocity. The mean scattering angle yields the function $p\beta/Z$ where p is the particle momentum, β is the particle velocity relative to the velocity of light, and Z is the particle charge. The method permits identification of π-mesons in the 20- to 150-M.e.v. energy range and of protons in the 70- to 1,000-M.e.v. energy range. Fifty-eight mass measurements, ranging in value from 200 to 450 m_e (electron masses), have a mean value of $(283 \pm 7)\ m_e$ and therefore are interpreted as representing π-mesons. (An independent check of the method was carried out with the tracks of π-mesons which were separately identified by their decay into μ-mesons, and with the tracks of μ-mesons which were separately identified by their decay into electrons. The masses of the two types of meson are roughly resolved by the technique although the errors in individual mass measurements are fairly large compared to the difference in mass of π- and μ-mesons.)

For particles ionizing at less than four times the minimum for a singly charged particle, Camerini, *et al.*, found the following percentages produced in nuclear interactions: π-mesons: 36 ± 2.5; protons: 51 ± 2.9; deuterons or tritons: 13 ± 1.5. For particles ionizing less than 1.5 times the minimum, they estimated: π-mesons: 79 ± 6; protons: 17 ± 3; deuterons or tritons: 4.0 ± 1.3. The differential energy spectrum for π-mesons was found to have a maximum at about 2 M.e.v. and to follow a power law of the form $dE/E^{1.5}$ in the energy range 250 to 1,400 M.e.v. The differential energy spectrum for protons was found to follow a power law of the form $dE/E^{2.5}$ for energies in the neighborhood of 1,000 M.e.v.

An experiment designed to verify that the mesons which are directly produced in high energy nuclear interactions are π-mesons was undertaken by Piccioni (29). The experiment was carried out at an elevation of 3,100 m. (Berthoud Pass, Colorado). Mesons occurring in coincidence with penetrating showers were detected by π-μ-e and μ-e delayed coincidences. The penetrating shower detector consisted of the following arrangement of Geiger counters. A tray of six counters (A) was covered by about 5 in. of

lead. A tray of ten counters (B) was placed below tray A and was separated from it by $8\frac{1}{2}$ in. of lead; $1\frac{1}{2}$ in. of lead was placed below tray B. The six A counters were separated from each other by $1\frac{1}{2}$ in. of lead to eliminate double coincidences which might be produced by μ-mesons accompanied by their knock-on secondaries. A penetrating shower was defined as a double coincidence in tray A, accompanied by a prompt coincidence in tray B. A coincidence of this type (designated A_2B) indicates the presence of two charged particles in tray A, one of which is capable of crossing the $8\frac{1}{2}$ in. of lead to reach tray B. These particles are presumably produced in a nuclear disintegration in the 5-in. lead layer above tray A; less than 8 per cent of these coincidences are produced by large air showers. The measured altitude dependence, between sea level and 3,100 m. elevation, supports the view that the majority of coincidences A_2B is due to local penetrating showers. A coincidence of one counter in tray A and one in tray B (designated AB) indicates a single penetrating particle incident on the apparatus.

A delayed coincidence tray of 12 counters (C) was placed below the penetrating shower detector and separated from it by 4 in. of carbon or sulfur. Below tray C was placed 5 in. of the same absorber. The carbon or sulfur served as a stopping layer for the mesons, the decay electrons being registered by a multichannel delay circuit, which recorded pulses in tray C which followed coincidences of type AB or A_2B by more than 1.3 and less than 8.4 μ sec. Separate channels were provided for four time intervals (1.3 to 3.3 μ sec., 3.04 to 5.04 μ sec., 4.76 to 6.76 μ sec., and 6.51 to 8.51 μ sec.) in order to verify that the events detected were indeed the decays of mesons. For delayed coincidences of both types, ABC_{del} and A_2BC_{del}, graphs of these data show an exponential decrease in frequency of events with increasing delay time, consistent with a mean life of 2.2 μ sec. This verifies that the delayed coincidences are indeed those corresponding to μ-e decay. The coincidences can be due to either π-μ-e or μ-e decays because the mean life for π-μ decay is so much shorter than that for the μ-e decay. In this experiment the distinction between the two decay processes is based upon the relative numbers of delayed coincidences found when the mesons stop in the different absorbers, carbon and sulfur.

This distinction arises as follows. In both carbon and sulfur, the positive π-meson will undergo decay into a μ-meson which subsequently will decay into an electron and be recorded, while the negative π-meson will undergo nuclear capture before it has time to decay and will not be recorded. One would therefore expect to have the same number of delayed coincidences in carbon as in sulfur for π-mesons stopping in the absorber.

On the other hand, when μ-mesons stop in carbon, practically all of the negative mesons decay, while in sulfur 72 per cent of them undergo nuclear capture, the remaining 28 per cent decaying with a mean life of 0.55 μ sec. (30). Because the minimum delay time registered was 1.3 μ sec., only 2.8 per cent of the negative μ-mesons were registered in sulfur. For this same minimum delay time, 60 per cent of the positive μ-mesons were recorded in

both materials. Therefore, within the accuracy of the experiment, one can say that all of the observed μ-decays in sulfur are due to positive particles. The ratio of the delayed-coincidence rates in carbon and in sulfur (designated C/S) must depend also upon the relative numbers of positive and negative μ-mesons which fall on the absorber. If one assumes, consistent with other experiments, that mesons are produced with a positive excess of 20 per cent, the ratio C/S should be 1.8 for μ-mesons.[2]

Delayed coincidences of the type ABC_{del}, corresponding to single mesons falling on the apparatus and undergoing decay in the absorber, give an experimental ratio $C/S = 1.85 \pm 0.05$. Delayed coincidences of the type A_2BC_{del}, which correspond to mesons produced in nuclear disintegrations in the lead above the detector, give a ratio $C/S = 1.11 \pm 0.1$. These data are consistent with the assumptions that mesons falling on the apparatus from above are predominantly μ-mesons, while those produced in nuclear disintegrations occurring in the apparatus are predominantly π-mesons.

Neutral π-mesons.—Evidence for the production of neutral π-mesons in nuclear interactions of great energy has been uncovered with the observations by several investigators of pairs of electrons and of electron showers associated with the interactions (31, 32, 33). The electrons are not produced directly in the interactions, but are presumably the result of materialization by high energy photons, themselves the decay products of neutral mesons. This possibility is the more attractive because of the Berkeley observations (34) of pairs of electrons produced by photons which show a Doppler shift of frequency indicative of their production by the decay in flight of artificially produced neutral π-mesons.

In cosmic-ray nuclear disintegrations, these electrons appear among the well-collimated particles (sometimes called "shower particles") which are produced. The electrons of a pair diverge at a very small angle ($\sim 0.2°$) with each other and travel roughly parallel to the shower particles. Carlson, Hooper & King (32) made a statistical analysis for 96 of these pairs which were observed in nuclear research emulsions exposed at 17,000 m. altitude. In order to permit energy measurements on the basis of scattering angle measurements, a criterion for choosing data was set to require that both electrons of a pair have a minimum track length of 1,000 μ in the emulsion. For energies less than 600 M.e.v., this results in a probable error in the energy of a pair of less than 30 per cent.

The small angle between the electrons of a pair makes it possible to establish within 0.2° the direction of travel of the photon which produced them. The observed directions of the electron pairs indicates that the photons have an angular distribution which is roughly isotropic in the lower hemisphere, very few being directed upward.

[2] μ-Mesons, of course, result from π-meson decay; it is therefore important to note that, of the π-mesons produced in the apparatus and having ranges such that they would stop in the absorber, only about 5 per cent will decay in flight, 95 per cent after stopping.

A differential energy distribution curve was obtained for the electron pairs; this curve then represents the distribution for the photons which produced the electrons. The curve shows a maximum of intensity near 75 M.e.v. The analysis by which the investigators inferred that the photons are the decay products of neutral π-mesons will be discussed briefly.

Under the assumption that the photons are emitted isotropically in a coördinate system moving at the velocity of the decaying mesons, it is possible to derive for the photons a theoretical energy distribution curve. The general features of this curve depend principally upon the Doppler effect, not essentially on the exact form of the energy distribution curve for the

TABLE VI

MEASUREMENTS OF THE NEUTRAL MESON MASS FROM THE OBSERVED ENERGY DISTRIBUTION OF THE PHOTONS*

Weights (No. of Pairs)	E_1	E_2	$\sqrt{E_1E_2}$
26	63	91	75.5
22	53	106	75.0
18	45	124	75.0
14	39	156	78.0
10	31	200	79.0
6	21	274	75.5
Total 96	Weighted mean: 75.8 M.e.v.		

* Energies are expressed in M.e.v. The mass of the neutral particle is $295 \pm 20\ m_e$.

decaying mesons. (When the neutral meson spectrum is assumed to be the same as that of the charged π-meson spectrum, the calculated curve for the photons is consistent with the experimental data.) The theoretical distribution shows a rise to a maximum intensity and a decrease in intensity at greater energies. It is possible to show that the rest mass of the decaying meson is related to the photon energy spectrum by the formula

$$m_0c^2 = 2\sqrt{E_1E_2}$$

where E_1 and E_2 are any two values of the photon energy corresponding to a single intensity less than the maximum. This formula is independent of the exact form chosen for the energy spectrum; it results from the Doppler effect. Table VI shows corresponding energy values taken from the smoothed experimental curve. The weighted mean value obtained for the meson rest mass is $m_0 = 295 \pm 20\ m_e$. This value compares favorably with the results of Panofsky, Aamodt & York (35) for gamma rays observed in cyclotron bombardment at Berkeley and there interpreted to be the decay products of a neutral π-meson.

The above analysis suggests that most of the photons at an altitude of 17,000 m. are the direct result of neutral meson decay, and not the result of other processes. The mass value would not be expected to lie close to its true value if the decay photons were diluted with a large proportion of photons from other sources.

An estimate of the relative numbers of neutral mesons produced in nuclear interactions was obtained from these experiments by an analysis which will not be reproduced here. The ratio of neutral to charged mesons was found to be 0.45 ± 0.10. This value suggests that, on the average, for each two charged mesons which are created in an interaction, one neutral meson is produced. This result therefore supports the view that the soft component of the secondary cosmic radiation, which represents a large fraction of the total energy at intermediate altitudes, is produced as a by-product of the nuclear interactions which take place at the top of the atmosphere. This view is further supported by observations of Camerini, Fowler, Lock & Muirhead (36) and of Green & Fretter (37) who find that there is an apparent loss of energy in nuclear disintegrations when the primary particle energy and the total energy of the secondary particles is compared. The creation of significant numbers of neutral π-mesons may account for this apparent energy loss.

Multiplicity and Angular Distribution of Mesons Produced in Nuclear Interactions

There exist abundant experimental data that show that several charged mesons can be produced in a single nuclear interaction. The multiplicity of production depends upon the energy and mass number of the bombarding particle, and the mass number of the struck nucleus. The average number of mesons produced in the more commonly observed interactions is less than 10; a few events which show much higher multiplicities have been reported.

The detailed nature of the nucleon-nucleon collisions within the nucleus is of considerable importance in the formulation of a suitable theory to describe the process. In particular, it is necessary to know whether several mesons are produced in a single nucleon-nucleon collision (so-called "multiple" production) or whether several collisions take place within the same nucleus, each resulting in the production of a single meson (so-called "plural" production). Some of the data discussed below indicate that multiple production takes place and that, at least for heavy nuclei, more than one inelastic nucleon-nucleon collision can take place, resulting in a "plural-multiple" production process.[3]

Salant, Hornbostel, Fisk & Smith (38) used the latitude effect to study the variation of multiplicity of meson production with the average energy of the bombarding particles. Ilford G5 and Eastman NTB3 nuclear research

[3] The term "cascade" is sometimes used to describe plural production and plural-multiple production. The term is avoided here because it is sometimes used to denote successive interactions of a particle with different nuclei.

emulsions were exposed for 6 hr. at an altitude corresponding to 15 gm./cm.^{2} residual atmosphere. Data for 217 interactions at 31° N. geomagnetic latitude and 166 interactions at 57° N. geomagnetic latitude were analyzed according to star size. The size was defined according to the number H of heavily ionizing particles (which are mostly protons and alpha particles), without regard to the number of lightly ionizing (1.3 times the minimum ionization for singly charged particles) particles present. This classification results in a separation of the stars into those which are produced in the light elements carbon, nitrogen, and oxygen (stars having less than six prongs), and those produced in the heavy elements silver and bromine (stars having more than eight prongs). This interpretation is supported by auxiliary experiments with laminated emulsions.

TABLE VII

DATA OF SALANT, HORNBOSTEL, FISK & SMITH*

	2 to 5H $\bar{m}$	6 to 8H $\bar{m}$	$\geqq 9H$ $\bar{m}$
31° N.	3.0±0.5	3.4±0.4	5.2±0.4
57° N.	2.6±0.3	2.7±0.5	3.2±0.4
1 to 8 B.e.v.	2.5±0.4	2.4±0.6	2.7±0.5

* Mean multiplicities of shower particles, $\bar{m}$, for small stars ($H \leqq 5$) and large stars ($H \geqq 9$).

Table VII gives the observed mean multiplicities which were defined as the ratio $\bar{m} = L/N$ where L is the total number of minimum ionization tracks observed in N stars which show at least one minimum ionization track. The mean multiplicities for the 1- to 8-B.e.v. energy range were computed from the formula

$$\tfrac{1}{4}[5\bar{m}(\text{north}) - \bar{m}(\text{south})].$$

This follows from the assumption that 1/5 of the protons at 57° N. have energies above 8 B.e.v. and have essentially the same intensity and spectral distribution as those at 31° N. (39). (At latitudes 31° N. and 57° N. the magnetic cutoff energies for protons are 8 and 1 B.e.v., respectively, and the average proton kinetic energies are 14 and 3 B.e.v., respectively.)

For light nuclei the mean multiplicities do not vary with incident proton energies, a result which was interpreted as indicating that plural meson production is infrequent in light nuclei. For heavy nuclei, 1- to 8-B.e.v. protons give the same multiplicity as protons of higher energy give in light nuclei. Further, the mean multiplicities for heavy nuclei increase with increasing proton energies. These results were interpreted as indications of plural meson production in heavy nuclei. Finally, the result that 1- to 8-B.e.v. protons give the same multiplicity for all star sizes was interpreted as indicating that

protons of this energy produce their maximum number of mesons in a 12- to 16-nucleon system.

Feld, Lebow & Osborne (40) reported data on 15 nuclear interactions which are also consistent with the assumption that, for light nuclei, the observed mesons are produced by a single nucleon-nucleon collision, whereas in heavy nuclei plural-multiple collisions may occur. The experiments were done with Eastman NTB3 nuclear research emulsions exposed at 31° N. geomagnetic latitude at an altitude of 28,000 m. (15 gm./cm.^{2} residual atmosphere). Five of the stars were attributed to light nuclei carbon, nitrogen, and oxygen; and 10, to heavy nuclei silver and bromine. The meson multiplicity for the light nuclei ranged from 6 to 13; and for heavy nuclei, from 5 to 27, averaging 13. The angular distributions of the emitted mesons were compared with angular distributions predicted on the basis of a simple theory in which all the mesons were assumed to be produced in a single, completely inelastic nucleon-nucleon collision with spherically symmetric angular distribution in the center-of-mass system. The stars in light nuclei showed angular distributions consistent with the theory; the stars in heavy nuclei had a larger angular spread and thus are not explained by the simple theory. The investigators therefore suggested that, in heavy nuclei, meson production is plural-multiple.

Using a cloud chamber at sea level, Fretter (41) studied the multiplicity of meson production in a 6-in. lithium plate. He obtained photographs of 14 nuclear disintegrations produced in the plate. The data were obtained with the use of Geiger counter control, which required a coincidence of one and only one of five counters above the lithium plate with two counters below the cloud chamber. Thus, for nuclear disintegrations occurring in the lithium plate to be photographed, the counters required that there be produced at least two particles capable of penetrating $5\frac{1}{2}$ in. of lead inside the chamber and $\frac{1}{4}$ in. of lead below the chamber. Several of these interactions showed multiplicities of charged particles which are too large to be explained by plural production: e.g., in the largest observed event, there appear 13 charged secondaries of which 10 are penetrating particles (here defined as those capable of penetrating two $\frac{1}{2}$-in. lead plates without interaction). If a single charged meson is produced in each nucleon-nucleon collision, the maximum number of charged particles produced in lithium would be 12, 7 mesons and 5 protons. If neutral mesons are produced, even fewer charged particles would be observed. Fretter concluded that plural collisions with multiple production of two to five mesons per nucleon-nucleon collision could explain his data.

Freier & Ney (42), using a cloud chamber at 55° N. geomagnetic latitude and at 24 gm./cm.^{2} residual atmosphere, obtained multiplicities of 6.8 ± 2.0 in carbon, 5.5 ± 2.0 in lucite, and 10.1 ± 1.7 in lead. These data are the averages for 6 interactions in carbon, 4 in lucite, and 32 in lead. The angular distributions of particles were found to be about the same in lead as in lucite and carbon. The data were interpreted as indicating an average multiplicity

of about five for single nucleon-nucleon collisions, plural collisions being possible in lead.

Detailed data on a few very high energy nuclear interactions are available. Using Eastman NTB3 nuclear research emulsions at 30,000 m. altitude Kaplon, Peters & Bradt (43) photographed a nuclear interaction in which a relativistic alpha particle of energy estimated at 8×10^{12} e.v. struck a bromine or silver nucleus yielding a narrow-angle cone of 23 relativistic particles, a more diffuse cone of 33 relativistic particles, and 18 nonrelativistic particles, the latter carrying 23 units of charge and a total energy of 3 B.e.v. The large multiplicity was taken as evidence that three or four of the nucleons of the incident particle made separate collisions. The angular distribution of the particles is inconsistent with that to be expected for multiple meson production (in a single nucleon-nucleon collision) if the angular distribution is isotropic in the center-of-mass system. It was therefore suggested that this nuclear event involved plural-multiple production, unless the mesons are produced anisotropically in the center-of-mass system.

Leprince-Ringuet, Bousser, Hoang-Tchang-Fong, Jauneau & Morellet (3) inferred similar conclusions from a nuclear disintegration obtained in an Ilford G5 nuclear research emulsion exposed at 30,000 m. altitude. This event showed 27 nonrelativistic prongs (consisting of protons, alpha particles, and larger fragments of nuclei) and 27 collimated relativistic particles. An analysis of the event indicated that the relativistic particles consisted of about 17 mesons and 10 protons.

Using Ilford G5 nuclear research emulsions exposed at 29,000 m. altitude for 16 hr., Lord, Fainberg & Schein (44) obtained a photograph of a large interaction which they interpreted as being produced by a single nucleon-nucleon collision because only two nonrelativistic protons were produced: one, a heavily ionizing particle that could be a 10-M.e.v. proton; the other, a 1,200-M.e.v. proton. In addition the event showed seven relativistic particles in a narrow cone of 0.003-rad. half-width, and eight relativistic particles in a more diffuse cone of 0.13-rad. half-width. Scattering measurements indicated momenta greater than 250 B.e.v./c for five of the particles in the narrow cone, and greater than 50 B.e.v./c for the other two. Two of the particles in the more diffuse cone had momenta of about 3 B.e.v./c. The energy of the initiating particle, believed to be a proton, was estimated to be about 3×10^{13} e.v., on the basis of mean scattering measurements.

The observed angular distribution of the particles shows the distribution in the center-of-mass system to be anisotropic. The distribution is consistent with one suggested by a recent theory proposed by Fermi (45). Described quite roughly, this theory is based on the assumption that, in the center-of-mass system, the nucleons move toward each other with a large Lorentz contraction along their line of relative motion and make an inelastic collision that is not head on. In order that angular momentum be conserved, the meson emission must then occur in two cones, one in the forward, the other in the backward direction of the incident particle. A transformation of this

angular distribution to the laboratory system results in a narrow cone and a more diffuse cone, which are observed. For an incident particle energy of 3×10^{13} e.v. the half-angle of the cones in the center-of-mass system must be about 40° to fit the interaction observed by Lord, *et al.*

The Possible Existence of τ-Mesons

Since 1944, when Leprince-Ringuet and Lhéritier (46) reported a cloud chamber photograph which seemed to indicate the existence of a positively charged particle having a mass value of about 1,000 m_e, there has been much discussion concerning the possible existence of such particles. These have been provisionally called τ-mesons. The principal objections to acceptance of their existence have been the lack of supporting evidence and the lack of information on their relation to other particles. Leprince-Ringuet's photograph has been discussed at some length. It records a rather rare phenomenon —the elastic collision of a high energy particle with an electron, with resulting transfer of an appreciable amount of energy to the latter. In principle such a photograph should lead to an accurate determination of the mass of the primary particle. Bethe discussed this case (47), together with several other meson mass measurements, in order to determine whether the mass of the particle might reasonably lie outside the reported limiting values of 870 and 1,110 m_e. He concluded that multiple scattering of the particle by the gas in the cloud chamber might push the lower limit to 600 m_e. On the other hand, in order to raise the upper limit to the proton mass value, he found it necessary to double all probable errors and add them together with the same sign. Because of the outside possibility that a coincidence of errors might have occurred, a final judgment based on this one photograph is not possible.

Other investigators have presented additional evidence suggesting the existence of τ-mesons. These data have taken the form of mass measurements or estimates made by use of the following methods: (*a*) Simultaneous measurement of momentum and range; (*b*) simultaneous measurement of momentum and ionization; (*c*) use of the law of conservation of mass and energy when the particle produces a nuclear interaction.

Systematic studies to determine the masses of cosmic-ray particles have been made by several investigators, using essentially the same momentum-range method, but with variations which materially affect the accuracy and usefulness of the results. In this type of experiment, particle detectors (Geiger counters, nuclear research emulsions, or cloud chambers) are placed outside a magnetic field to define the paths of the particles before they enter and after they leave the magnetic field. From measurements of the angular deflections the particle momenta can be determined. Retallack & Brode (48) used a pair of cloud chambers for deflection measurements and a third chamber containing lead plates for range measurements. Alikhanyan, Alikhanov, *et al.* (49) used pairs of Geiger counters for deflection measurements and other Geiger counters to measure ranges in a lead absorber. Franzinetti (50) and Barbour (51) used nuclear research emulsions on two sides of a mag-

netic field for deflection measurements and observed ranges in the second emulsion.

The most recently reported of these experiments, *viz.*, those of Barbour and of Franzinetti, report no evidence for particles having mass values intermediate between π-meson and proton masses, i.e., no evidence for the existence of τ-mesons. Barbour's data were obtained at an altitude of 29,000 m; Franzinetti's data, at 3,350 m. The latter data are particularly interesting and significant because of the fact that secondary particles which may be produced by a particle at the end of its range can be observed in the emulsion. This possibility does not exist for the other methods mentioned. Franzinetti reported only seven mass measurements in a total of 360 which might be interpreted as supporting evidence for the existence of τ-mesons. None of these particles showed evidence of spontaneous decay at the end of its range. All but one was positively charged. In an analysis of the data, Franzinetti pointed out that elastic scattering of a particle in the gas between the emulsions can occasionally produce a spurious mass measurement which would go undetected. (A criterion that the entrance and exit directions of motion of a particle be tangent to a circle was used to eliminate most of these cases. However, a small proportion of scattered particles could survive this test if, for example, they were scattered near the midpoints of their trajectories.) Under the conditions of his experiments, Franzinetti concluded that fortuitous coincidences of tracks could be expected to lead to spurious mass values in perhaps three or four cases. To these and other possible uncontrollable errors, he attributed the seven intermediate mass values. It is particularly significant that all but one of these are positively charged and that none shows any evidence of spontaneous decay at the end of its range—a strong inference that these are, in reality, proton tracks. Franzinetti concluded that his own experiments indicate that the existence of τ-mesons must be accepted only with great reserve, adding that if his experiments do indicate the existence of such, they are present at 3,350 m. elevation with a frequency less than three per cent of that of π- and μ-mesons.

Butler, Rosser & Barker (52) obtained three cloud chamber photographs which they tentatively identified as τ-mesons. Mass estimates were made on the basis of estimated ionization and the measured momenta of the particles in a 7,500-gauss magnetic field. All of the particles were associated with penetrating showers.

In one photograph a positively charged particle of momentum $(1.1 \pm 0.1) \times 10^8$ e.v./c was observed as a product of a three-pronged star, which was produced in the gas of the chamber by a nonionizing particle. The momentum measurement is particularly good because the track length in the chamber is quite long. The ionization of the particle was 6 to 10 times the minimum for singly charged particles. These data yield a mass value in the range 650 to 900 m_e. In contrast, a proton of this momentum would ionize 36 times the minimum; a meson, 2 times the minimum.

The second example also showed a positively charged particle. Its track was free of visible distortion and appeared in the chamber close to a proton

track of momentum 3.6×10^9 e.v./c and ionization 4 to 5 times the minimum, permitting a comparison of ionization estimates. An observed momentum of $(1.7\pm0.2)\times10^8$ e.v./c and ionization of 5 to 7 times the minimum placed the mass at $(1{,}000\pm200)m_e$. A proton of this momentum would ionize 15 times the minimum; a π-meson, 1.2 times the minimum.

The charge of the third particle was negative. Its momentum and ionization were, respectively $(1.7\pm0.2)\times10^8$ e.v./c and 4 to 6 times the minimum, yielding a mass in the range 800 to 1,020 m_e. A meson of this momentum would ionize at the minimum; a proton, at 15 times the minimum.

Three examples of stars which may have been produced by τ-mesons have been observed in nuclear research emulsions. In each case it was possible to identify which was the initiating particle and to measure the total kinetic energy of the other particles. It is essential to the method that the direction of the initiating particle be positively established. Particle scattering and track grain density, both increasing in the direction of the star origin, permit this to be done. Because the initiating particle stops before striking the nucleus, the binding energies and the kinetic energies of the observed particles must be supplied by the mass-energy of the initiating particle. A lower limit for the particle's mass can thus be determined.

Leprince-Ringuet (53) observed a double star in a nuclear research emulsion exposed at 4,300 m. elevation (Mont Blanc). A particle, showing increasing scattering and grain density as it stopped, produced a six-prong star, one of whose products was a π-meson which stopped and produced the second star. The total energy liberated in the first star indicated a mass exceeding $700m_e$ for the particle initiating the first star. (The method leads to a lower limit for the mass because neutral, and therefore unobservable, particles may also be produced in the star.)

Harding (54) observed a three-prong star produced by a particle which showed increasing scattering and grain density as it approached the star. The three secondary prongs were coplanar. The total excitation energy depends upon the identification of the star prongs, a difficult matter in this case because the emulsion was exposed for 85 days, and so the fading of the latent image might have been serious. The observed grain density of the initiating particle was, however, greater than that of a π-meson. If the three prongs are protons, the minimum total excitation energy is 510 M.e.v., too great for a π-meson. If the three prongs are those of π-mesons, the total excitation energy is 535 M.e.v., corresponding to a mass of about 1,000 m_e. (The observed grain density is too small for this value, requiring the assumption that considerable fading must have taken place.)

Forster (55) found a star of similar type which was produced in an emulsion exposed at 9,400 m. altitude for a few hours. The star was produced by a charged particle that traveled 50 μ in the emulsion and showed increasing ionization along its track in the direction of the star. Ten charged particles were produced in the star. These were identified as five protons, one deuteron, three alpha particles, and one π- or μ-meson. The sum of the kinetic and binding energies of the particles (107 M.e.v.), together with the rest mass of the

meson (assumed to be a π-meson), yields a minimum mass of 500 m_e for the initiating particle. Unseen neutral particles might well increase this value by 200 m_e.

The evidence for the existence of τ-mesons does not yet seem to be conclusive. On the other hand, the evidence cannot be lightly dismissed. The few direct mass estimates indicate the existence of charged particles of mass 1,000 m_e. If the star data relate to the same particles, then the positively charged τ-mesons must interact with nuclei. There is little evidence to relate these particles to other, well-established ones. It is possible that further investigation may show a relationship between τ-mesons and the V-particles, which are discussed below.

It is disturbing that the systematic work on the masses of particles has not yielded positive evidence for τ-mesons; indeed, the evidence is negative, if anything. However, it should be pointed out that the experimental techniques so far used may bias against the possibility of observing τ-mesons under conditions suitable for mass measurements. As a case in point, one may cite the μ-meson, for which large numbers of mass measurements were not available until many years after its initial discovery.

V-Particles

In 1947 Rochester & Butler (56) reported cloud chamber photographs of two remarkable events, both associated with penetrating showers. Each photograph showed two tracks diverging at a large angle with each other from a common point in the chamber gas. The photographs differed in that in one, the tracks diverged at an acute angle in the downward direction, while in the other the tracks diverged at an obtuse angle, one track going in the upward direction and the other going in the downward direction. Rochester & Butler interpreted the first event as the spontaneous decay of a neutral particle, and the second as the spontaneous decay of a charged particle, both particles being of new types. P. M. S. Blackett has suggested that these particles be called, provisionally, "V-particles" until such time as they are fully identified.

Seriff, Leighton, Hsiao, Cowan & Anderson (57) obtained 34 cloud chamber photographs of V-particle decays which confirm the conclusions of Rochester & Butler and give information on the lifetimes of the V-particles and the nature of the decay products. Of these 34 photographs, only 4 show charged V-particles, so that the available information on the charged type is meagre. The remaining 30 photographs shed much light on the nature of neutral V-particles.

The evidence thus far reported indicates that the neutral V-particle is produced in a high energy nuclear event. It then decays in flight, the mean rest lifetime being about 3×10^{-10} sec. The observed decay products are two charged particles, one positive and one negative; possibly one or more neutral particles are also produced. In no cloud chamber photograph has it been possible to identify simultaneously both of the charged decay products. However, it is now definitely established that both positive and negative particles,

smaller in mass than protons and greater in mass than electrons, are observed. Some of these have been identified as having masses in the π- and μ-meson mass range. Also are observed particles which could have masses as large as the proton.

Hopper & Biswas (58) reported one nuclear research emulsion observation of a neutral V-particle decay in which the masses of both decay products were determined by means of scattering measurements. One was identified as a proton; the other, as a π- or μ-meson. No determination of the charge signs was possible in this observation. It thus appears that the decay products include both protons and mesons. It is not yet known whether each decay yields one proton and one meson, or whether sometimes just two mesons result. Because positive as well as negative mesons have been observed among the decay products, it is apparent that there must be decays yielding two mesons unless one admits the existence of negative protons. That the latter may soon be identified is an exciting possibility.

A more detailed discussion of the data of Seriff *et al.* (57) on neutral V-particles follows. The angles between pairs of tracks lie between 3.5 and 126°. For most of the particles the ionization is indistinguishable from the minimum for singly charged particles, and the momenta are greater than 200 M.e.v./*c*. In a few cases the ionization and curvature permit partial identification of the particles. One was observed to have a mass lying in the range 150 to 350 m_e. In each of five other decays, one of the decay products was observed to have a mass less than the proton mass. It is unlikely that the decay products have masses as light as the electron because those that have been observed to cross 2-cm. lead plates have shown no energy loss by radiative collisions; in three cases both decay products penetrated the lead plate, and in three other cases, one of the decay products penetrated the plate.

There is evidence that at least one of the decay products has a strong nuclear interaction. In one case a particle was observed to be deflected through an angle of 35° in the lead plate. In another a particle was observed to produce a nuclear disintegration. In eight other cases, nuclear processes are not required to explain the observed deflections, which were all less than 10°.

The possibility that neutral particles are also emitted in the decay process cannot be ruled out. In some photographs it was possible to establish, by means of the orientations of associated particle tracks, the point at which the unstable V-particle was produced in a parent nuclear event. If only two decay products, *viz.*, the observed charged particles, are produced, their plane should contain this point. Within the accuracy of the measurements, this was indeed the case for 12 of 15 events in which associated particles permitted location of their point of origin. The remaining three events might not have come from the nuclear event that produced their associated particles. While these data strongly suggest a two-particle decay, the accuracy of the measurements is not sufficient to rule out the possible presence of neutral decay particles.

On the natural assumption that the V-particle decay is spontaneous, and therefore of a random nature, one can compute a mean lifetime from the indirectly observed path lengths and momenta of the V-particles. The direction of travel of the V-particle, and hence its path length in the sensitive region of the chamber, can be determined from the location of the parent nuclear impact or from the momenta of the decay particles. Since the decay would have been observed had it occurred at any point along this path length, this length in the chamber gives the distance which the particle is observed to go prior to decaying. The observed lifetime, computed from the path length, must then be corrected in each case for the relativistic time dilation factor. The mean rest lifetime is, of course, independent of the fact that the lifetime in each case is measured from the time at which the V-particle entered the chamber, for the mean lifetime of any group of particles subject to random decay is independent of the origin of time measurement. Using this technique, the Pasadena group estimated the V-particle lifetime to be $(3 \pm 2) \times 10^{-10}$ sec.

The existing data give little information on the charged V-particles. Two cases in which the secondary particle penetrated lead plates without energy loss by radiative collision indicate that the mass of the secondary is greater than the electron mass. There are indications that the neutral and the charged V-particles are produced in roughly equal numbers although the charged particles probably have a shorter lifetime.

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MASS AND RELATIVE ABUNDANCE OF ISOTOPES[1]

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The history of the measurement of isotopic masses and abundances parallels closely the history of the development of vacuum and electronic techniques. Today, practically all determinations of isotopic masses and abundances are made with mass spectrometers or mass spectrographs, and the modern versions of these instruments lean heavily upon the latest techniques in the vacuum and electronic fields.

The isotopic Tables of 1933 are made up almost exclusively of the mass spectrographic measurements of Aston (1). Both packing fractions and isotopic abundances were determined by allowing ion beams to impinge on photographic plates and observing the position and intensities of the lines found on the developed plates. Only in the early work of Dempster (2) was any serious systematic attempt made to measure isotopic abundances by electrical means.

The techniques employed by Smyth (3), Bleakney (4), Tate & Smith (5), and others in the studies of impact of gases by electrons were soon applied in isotopic abundance studies, and in 1932 Bleakney (6) and his co-workers began reporting isotopic abundance measurements with an instrument using a common magnetic field for collimating the electron beam and making a mass analysis of the ions produced by electron impact. The use of this type of instrument was extended, by Nier (7) and others, so that by 1942 when the second edition of Aston's book appeared, of the 83 naturally occurring elements, 48 had been measured by electrical means. During the war years few isotope abundance measurements were made, but by the end of 1949 electrical abundance measurements had been made in 73 of the 83 elements reported in Tables. By the end of 1950 this number had grown to 78.

Whereas in 1930 Aston was the sole worker measuring precise atomic masses, the 1930's saw new workers enter the field. Included among these were Bainbridge (8), Dempster (9), Bainbridge & Jordan (10), Mattauch (11), and Jordan (12). Each name or combination of names is associated with a particular type of instrument. For example, to a mass spectroscopist, a Bainbridge & Jordan instrument means a double focusing mass spectrograph employing a 127° electrostatic analyzer followed by a 60° magnetic analyzer.

The 1930's also saw the firm adoption of the "doublet method" for the determination of atomic masses. In this method the mass difference between two atomic or molecular ion fragments having the same mass number is found. The determination of a number of such doublets, at least one of them containing O^{16}, permits the computation of the masses of the various isotopes

[1] This review is essentially a survey of papers published in 1950.

appearing in the doublets, $O^{16} = 16.00000$ being used as the standard for the measurements. Because comparisons are always made between ions having nearly the same mass, instrumental errors are minimized.

During the early 1940's few isotopic mass measurements were made. Okuda (13, 14, 15) and his colleagues, using a Bainbridge-Jordan type instrument, measured the packing fractions of chlorine, argon, iron, nickel, sulfur, and titanium isotopes. In 1946 Ewald (16), using a Mattauch type instrument, gave new mass values for C^{13} and N^{15}.

It was not until 1949 that a serious interest in measuring atomic masses again arose. Shaw (17), using a Dempster instrument, redetermined the masses of the nickel isotopes. Ogata (18), with his Bainbridge-Jordan type instrument, reported on isotopic weights of some medium elements. Nier, Roberts & Franklin (19) reported on a new double focusing mass spectrometer capable of giving highly precise mass values. Duckworth (20) began a long series of measurements of mass doublets with a determination of the packing fraction difference Pt^{195}—Cu^{65}.

Mass Measurements in 1950

Mass spectrographic determinations.—It has always been a source of some surprise to the writer that so little interest in the measurement of atomic masses has been shown. Although the equivalence of mass and energy has long been known and the rough shape of the packing fraction curve for the elements was established early, next to nothing was known about whole regions of the curve let alone details of the fine structure. The relatively new interest shown in nuclear shell structure theories has added impetus to the work. Of special note are the many fine measurements being made by Professor H. E. Duckworth and his students of Wesleyan University. With a Dempster type apparatus, Duckworth and his students made many mass measurements during 1950 and filled numerous gaps in the packing fraction curve.

Table I gives the packing fractions and associated atomic masses measured by Duckworth and his associates. Since many of Duckworth's determinations are based upon comparisons with hydrocarbon fragments they are dependent upon the mass values taken for H^1 and C^{12}. Because recent work in the writer's laboratory indicates that the previously accepted masses of H^1 and C^{12} in all likelihood need revision, the published results of Duckworth and his associates have been revised here to take into account the new H^1 and C^{12} values which are given later in this chapter.

Ewald,[21] using a Mattauch type instrument, carefully measured the doublet D_2—He^4 and found the value $(256.04 \pm 0.08) \times 10^{-4}$ AMU.[2] The close agreement between this and the value 256.12 ± 0.09 listed in Table II is especially gratifying since the apparatus employed in the two researches was so different.

[2] Atomic mass units.

TABLE I

PACKING FRACTIONS AND ISOTOPIC MASSES DETERMINED IN 1950 BY DUCKWORTH AND COLLEAGUES BY MASS SPECTROGRAPHIC MEANS
[Values are based on masses of H^1 and C^{12} found in TABLE II]

Nuclide	Packing Fraction $\times 10^4$	Mass	Reference
Si^{28}	-5.08 ± 0.03	27.98580 ± 9	73
Si^{29}	-4.91 ± 0.04	28.9858 ± 1	74
Si^{30}	-5.64 ± 0.05	29.98308 ± 16	75
S^{32}	-5.51 ± 0.03	31.9824 ± 1	76
Cr^{50}	-7.96 ± 0.05	49.9602 ± 3	77
Cr^{52}	-8.23 ± 0.05	51.9572 ± 3	77
Fe^{54}	-7.99 ± 0.04	53.9568 ± 2	77
Fe^{56}	-8.43 ± 0.02	55.9528 ± 1	73
Ni^{58}	-7.98 ± 0.03	57.9537 ± 2	73
Ni^{60}	-8.54 ± 0.05	59.9488 ± 3	74
Cu^{65}	-7.85 ± 0.04	64.9489 ± 3	74
Zr^{90}	-7.52 ± 0.07	89.9323 ± 6	75
Mo^{96}	-6.68 ± 0.03	95.9359 ± 3	75
Mo^{100}	-6.13 ± 0.03	99.9387 ± 3	75
Pd^{104}	-6.10 ± 0.04	103.9365 ± 4	77
Pd^{108}	-5.74 ± 0.05	107.9371 ± 3	77
Cd^{112}	-5.37 ± 0.03	111.9399 ± 3	73
Cd^{116}	-4.97 ± 0.04	115.9423 ± 4	73
Sn^{116}	-5.32 ± 0.03	115.9383 ± 4	73
Nd^{144}	-3.02 ± 0.05	143.9565 ± 7	78
Hf^{180}	0.08 ± 0.05	180.0014 ± 9	78
Pt^{195}	1.38 ± 0.03	195.027 ± 6	77

All of the above values are related to $O^{16} = 16.0000$ by mass spectrographic measurements alone. Packing fraction differences measured but from which masses can not be computed without use of disintegration data or older packing fraction difference measurements include the following: $W^{183} - Ni^{61} = 8.49 \pm 0.02$, $W^{186} - Ni^{62} = 9.03 \pm 0.02$, $Pt^{198} - Zn^{66} = 9.43 \pm 0.04$, $Pt^{192} - Zn^{64} = 9.24 \pm 0.03$*; $Cd^{110} - Mn^{55} = 2.53 \pm 0.03$†, $Cd^{114} - Fe^{57} = 2.88 \pm 0.03$†; $Pr^{141} - Ti^{47} = 3.67 \pm 0.03$, $Ba^{138} - Zr^{92} = 3.63 \pm 0.04$‡; $Pr^{141} - Mo^{94} = 3.54 \pm 0.05$.

From these doublets and mass differences computed from disintegration experiments, atomic mass values may be computed. Because of rather detailed and sometimes controversial considerations encountered, the reader is referred to the original references for the assumptions made and masses computed.

* See reference (74).

† See reference (73).

‡ See reference (78).

Mass Spectrometric Determinations

Prior to 1950, all atomic mass measurements made by ion mass analyses were performed with mass spectrographs, i.e., instruments in which the ions impinge on a photographic plate. Masses are computed from the positions of the lines on the developed plates. Several years ago it occurred to the writer that if one combined certain features of present-day mass spectrographs and mass spectrometers one would obtain an instrument which could measure masses with as high an accuracy as has ever been attained. Moreover, such an instrument has features which potentially permit even higher accuracy.

Figure 1 shows a schematic view of the essential parts of the apparatus used by Nier & Roberts (22, 23, 24) in measuring mass spectrometrically. Ions produced by electron impact or thermionic emission in the source of the main spectrometer tube are sent through the collimating slits S_1 and S_2 into a 90° electrostatic analyzer. An energy spectrum is produced in the focal plane containing the slit S_3. Refocusing occurs at S_4 after the ions have passed through the asymmetrical 60° magnetic analyzer. The ion currents are measured with a vibrating reed electrometer or electron multiplier and recorded by one of the channels of a Brush two-channel magnetic oscillograph.

In order to minimize the effect of fluctuations in the magnetic field or ion deflecting voltage, a second and smaller auxiliary mass spectrometer tube is mounted in the same magnetic field as employed for the larger one. This tube is very similar in construction to ones ordinarily used for isotope abundance measurements (25). It differs, however, in that a double collector system is used which is coupled to a differential amplifier. This tube is adjusted so that the ion current is split and half goes to each collector plate. Under these conditions there will be no output from the differential amplifier. If now, the magnetic field or accelerating voltage applied to the ions should change, the ion beam will shift and a signal will appear at the output of the differential amplifier. This signal is fed into the high voltage supply in a sense which tends to restore the ion beam to its original position. Since both spectrometer tubes obtain their ion accelerating and deflecting potentials from a common voltage divider, the action of the small tube corrects for fluctuations which would normally disturb the paths of ions in the main tube.

A mass spectrum in the main tube is obtained by varying resistance R, i.e., by moving the position of tap A. Since the auxiliary tube and the associated high voltage supply and divider constitute an inverse feed-back loop, it may readily be shown that the change in mass of ions collected in the main tube is related to the change ΔR in R by the relations

$$\Delta M/M = (\Delta R/R)[G/(G+1)] \qquad 1.$$

where G is the open circuit gain of the feed-back loop.

In an unpublished improvement on the instrument an integral control device has been placed between the differential amplifier and the high volt-

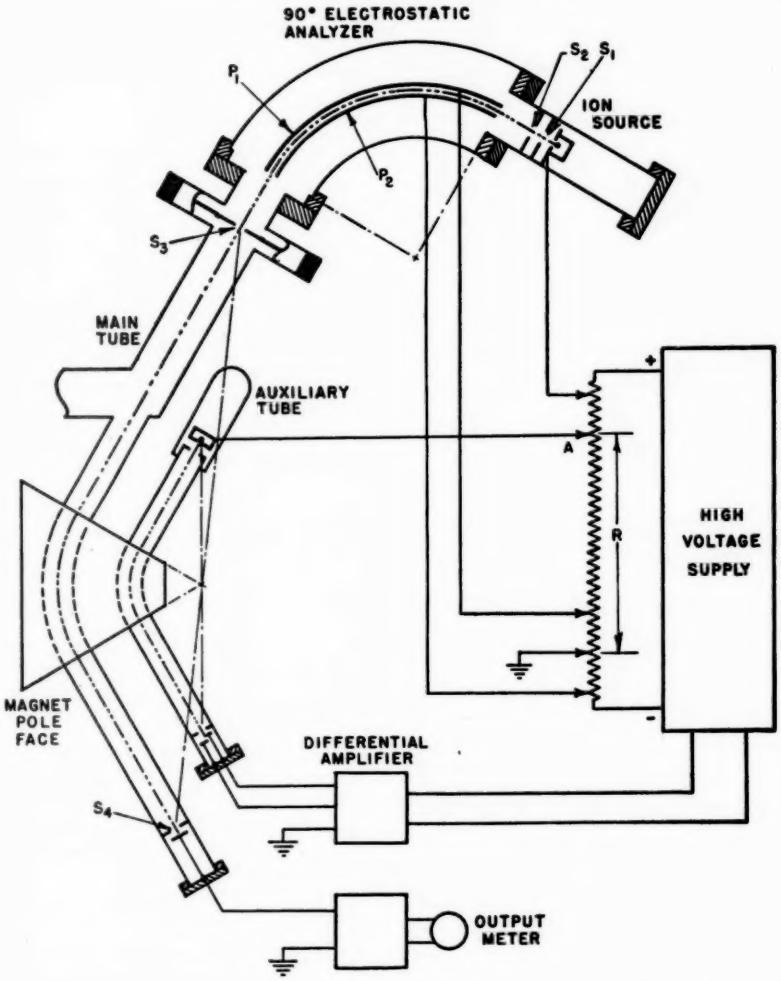

FIG. 1. Schematic drawing of mass spectrometer tubes showing action of regulation circuit. Mean radius of cylindrical electrostatic analyzer 18.87 cm. Separation of plates P_1 and P_2, 1 cm. Radius of magnetic analyzer in main and auxiliary tubes, 15.24 and 7.62 cm. respectively. Distances of S_3 and S_4 from effective pole faces are 34.77 and 20.73 cm., respectively. Asymmetrical construction reduces width of beam at S_4 owing to divergence of ion beam. S_1, S_2, S_3 and S_4 are 0.0025, 0.033, 0.25, 0.0025 cm., respectively, for most of data reported here. S_1 and S_2 are separated by 3.71 cm. Main and auxiliary tube ion accelerating potentials are approximately 4,000 and 1,000 v., respectively. Hence, gas used in auxiliary tube has approximately the same molecular weight as the doublet to be studied.

age supply. This operates from the output signal leaving the differential amplifier and acts to hold this signal at zero value. In effect, this gives the loop infinite gain as the spectrum is swept. The formula for computing mass differences then reduces to

$$\Delta M/M = \Delta R/R. \qquad 2.$$

The elimination of the need for measuring G not only greatly reduces the time required for making measurements but in addition improves the accuracy.

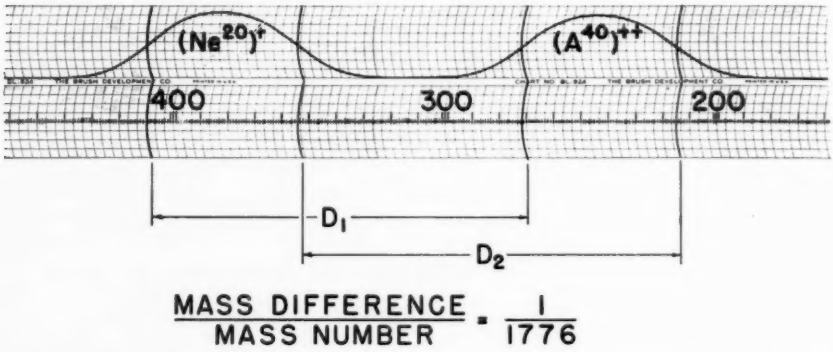

FIG. 2. Mass doublet $(Ne^{20})^+ - (A^{40})^{++}$. Numbers on chart give ohm reading of helical potentiometer used to sweep spectrum. R and ΔR are approximately 245,000 and 138 ohms respectively for this spectrum.

Figure 2 shows a typical chart obtained for the doublet $(Ne^{20})^+ — (A^{40})^{++}$ when a mixture of neon and argon was placed in the main tube. The second channel of the oscillograph simultaneously records the resistance of the potentiometer. Mass differences are found by measuring distance on charts between corresponding half-heights of peaks.

Table II gives the doublets studied and the values found for them. Values for H^1 and C^{12} were found by two completely independent doublet cycles. Roberts (23) measured the doublets H_2—D, $C^{12}H_4$—O^{16}, D_2O^{16}—$A^{40}/2$ and C_3H_4—A^{40}. From these he found $H^1 = 1.0081686 \pm 52$ and $C^{12} = 12.003803 \pm 13$. Nier (24) studied the doublets $(C^{12})_4$—$S^{32}O^{16}$, $(C^{12})_6(H^1)_4$—C^{12} $(S^{32})_2$ and the triple $(C^{12})_3$ $(H^1)_8$—$C^{12}(O^{16})_2$—$C^{12}S^{32}$ and found $H^1 = 1.008159 \pm 4$, $C^{12} = 12.003850 \pm 6$. The weighted average of these values together with other mass values computed from the doublets given in Table II are given in Table III. Previous values are given for comparison.

NEW INSTRUMENTS AND MISCELLANEOUS MASS DETERMINATIONS

The omegatron.—The use of cyclotron resonance has appealed to many as a method of measuring e/m of charged particles. Hipple, Sommer &

TABLE II

MASS DOUBLETS DETERMINED BY MASS SPECTROMETRY

Doublet	ΔM in 10^{-4} AMU
$D_2O^{16}-A^{40}/2$	419.67 ±0.18
$D_2O^{16}-Ne^{20}$	307.21 ±0.39
$Ne^{20}-A^{40}/2$	112.80 ±0.18
$(C^{12})_2H_4-C^{12}O^{16}$	364.43 ±0.22
$(N^{14})_2-C^{12}O^{16}$	112.80 ±0.13
$(C^{12})_3H_8-(N^{14})_2O^{16}$	617.6 ±0.9
$C^{12}H_4-O^{16}$	364.78 ±0.22
$C^{12}H_2-N^{14}$	125.86 ±0.13
$(C^{12})_3H_4-A^{40}$	688.77 ±0.35
$C^{12}H_4-Ca^{40}$	685.39 ±0.46
$Ca^{40}-A^{40}$	3.2 ±0.8
D_2-He^4	256.12 ±0.09
$(C^{12})_4-S^{32}O^{16}$	331.82 ±0.07
$C^{12}(O^{16})_2-C^{12}S^{32}$	177.82 ±0.25
$(C^{12})_3(H^1)_8-C^{12}(O^{16})_2$	729.67 ±0.41
$(C^{12})_6(H^1)_4-C^{12}(S^{32})_2$	873.26 ±0.58
H_2-D	15.519±0.017

TABLE III

COMPARISON BETWEEN ATOMIC MASSES OF LIGHT ISOTOPES MEASURED IN 1950 AND EARLIER ACCEPTED VALUES

[All 1950 results except that for He^4 are based on mass spectrometric determinations alone]

Isotope	Bainbridge Report*	1950 Determinations
n	1.0089383±57	1.009008± 5†
H^1	1.0081283±28	1.008165± 4
D	2.0147186±55	2.014778± 8
He^4	4.003880 ±32	4.003944±19‡
C^{12}	12.003856 ±19	12.003842± 6
N^{14}	14.007536 ±22	14.007564± 7
Ne^{20}	19.99872 ±13	19.998835±43
S^{32}		31.982218±25
A^{40}		39.97524 ± 3

* See ref. 79.

† Computed from H^1 and average $n-H^1$ difference found by averaging: 782±1.5 k.e.v. (80); 789±6 k.e.v. (81); 785±7 k.e.v. from H_2-D (Table II) and binding energy of deuteron 2.230±0.007 m.e.v. (82).

‡ Weighted Average of D_2-He^4 from ref. 21 and ref. 22 used in computing mass of He^4.

Thomas (26)[3] have developed an instrument which they call "the omegatron"; it has already proved useful in determining the ratio of the precessional frequency of the proton to the cyclotron frequency in the same magnetic field (27). The data obtained when combined with other information enables one to compute the proton moment in nuclear magnetons, the Faraday, and the ratio of the mass of the proton to that of the electron. The instrument appears promising as a means for measuring precise atomic masses, especially in the low mass range. Hipple and his colleagues have measured the H_2—D mass doublet and gave the tentative value $(15.45 \pm 0.08) \times 10^{-4}$ AMU for this doublet.

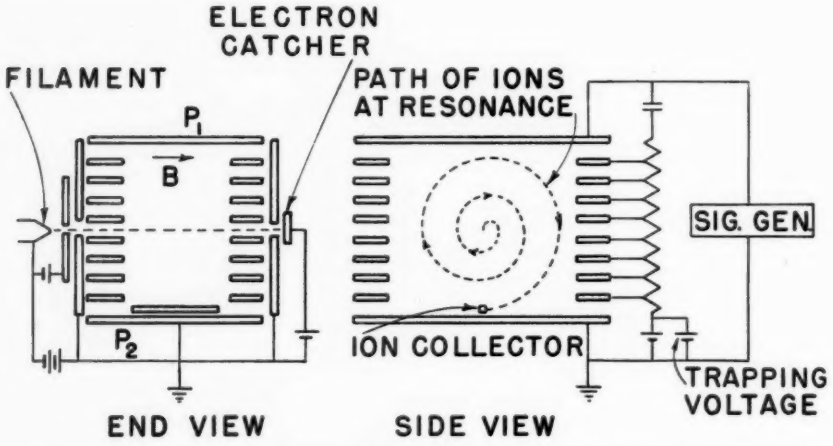

FIG. 3. Schematic view of omegatron. Plates P_1 and P_2 are 3×5 cm. and spaced 2 cm. apart. The entire apparatus including divider for the guard plates is placed in a 47 mm. O.D. glass tube and mounted between poles of an electromagnet. Operating pressure is usually below 10^{-6} mm. Hg and ion currents collected are about 3×10^{-14} amp.

Figure 3 shows two schematic views of the essential parts of the instrument. An electron beam (collimated by the uniform magnetic field B) leaves the filament and stops on the electron catcher. Plates P_1 and P_2 have impressed upon them a radio-frequency (r.f.) potential difference from the signal generator. Eight guard plates shown between P_1 and P_2 insure that the r.f. field between P_1 and P_2 is uniform. A direct current trapping voltage maintains all of the guard rings at a potential positive in respect to the plates P_1 and P_2 and retards the loss of ions in the axial direction. This permits the r.f. field to act on them over many cycles and hence makes the device tune sharply. If the impressed frequency is equal to the cyclotron frequency of the ions formed by the electron impact, the ions will pursue a spiral path and after many turns they will be caught on the ion collector.

[3] The writer is indebted to the authors for a copy of their manuscript prior to publication.

Figure 4 shows a mass spectrum produced at mass two. Due to radial electrostatic fields in the tube the observed resonance frequency differs slightly from the simple cyclotron formula $\omega = eB/M$. Radial fields are due to the trapping voltage and space charge. The effect is small and may be determined. It should not be an appreciable source of error in atomic mass determinations if the doublet method is used.

The chronotron.—The constancy of the angular velocity of particles of a given e/m in a given magnetic field has been utilized by Goudsmit (28)[4] in a "time of flight" instrument called the "chronotron." Accelerated ions enter-

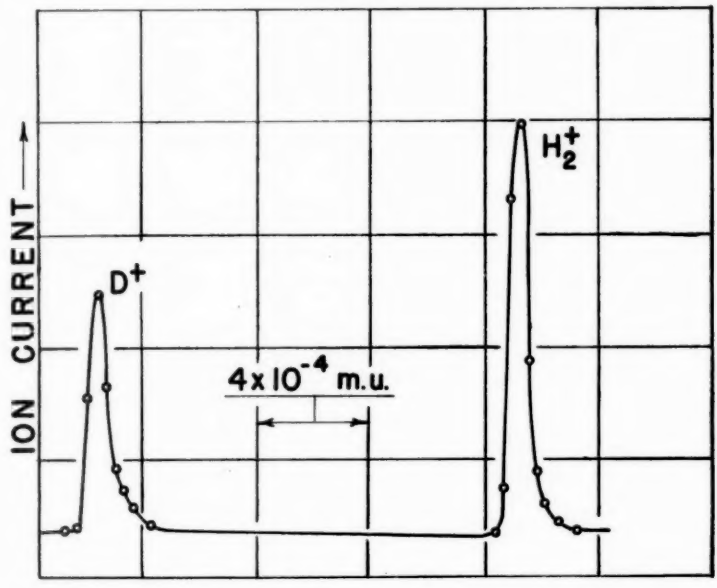

FIG. 4. Mass spectrum at mass 2 for mixture of H_2 and D_2. Electron current 3.0 μamp., pressure 6×10^{-7} mm. Hg, r.-f. voltage between P_1 and P_2 0.06 v. rms. Trapping voltage 0.06 v.

ing a uniform magnetic field with a component of velocity in the direction of the magnetic field will describe a helical path. The time per revolution in round numbers for singly charged ions is $T = 670\ M/B$ μsec. where M is the mass of the ion in atomic weight units and B the magnetic induction of the field in gauss.

With a magnet having a spherically shaped coil and powered by submarine storage batteries an instrument has been constructed for which the magnetic induction is around 400 gauss and the radius of curvature 5 in. The ion beam produced either by electron impact of a gas or thermionic

[4] The writer is indebted to Dr. Goudsmit for additional details giving the current status of the apparatus constructed by himself and his colleagues, P. I. Richards and E. E. Hays.

emission is pulsed for about $\frac{1}{4}$ μsec. to give ions of equal momentum rather than energy. Thus all ions will traverse roughly the same path through the magnetic field. As a collector, a Faraday cage, scintillation counter, and magnetic multiplier have been used. The latter appears to give the greatest sensitivity in the tests made.

The geometric construction of the model constructed permits the observation of ions which have made up to six revolutions before reaching the collector. With a timing system adopted from Loran, time may be measured

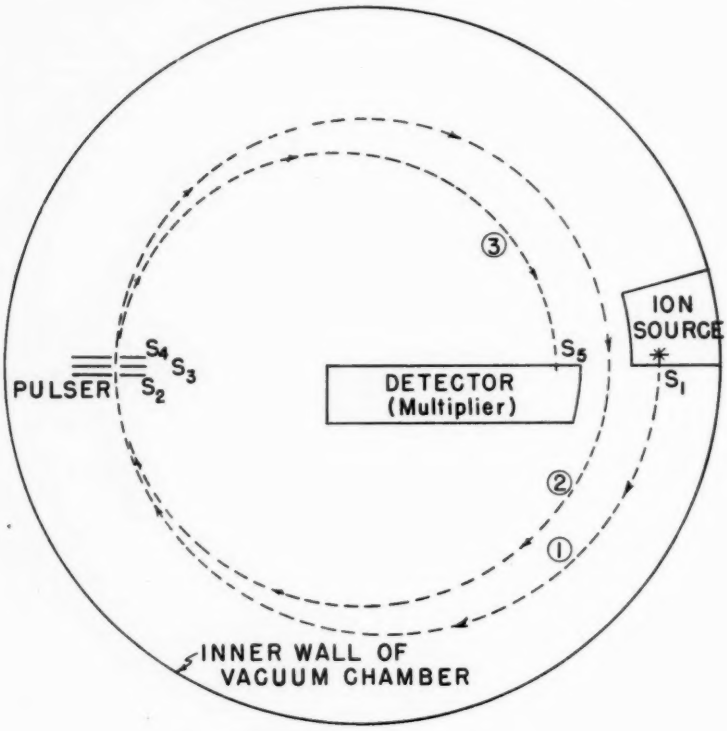

FIG. 5. Cross section of synchrometer.

to 0.01 μsec. For ions which have made six revolutions in the field of 400 gauss the dispersion is approximately 10 μsec. per mass unit, i.e., mass measurements may be made to one millimass unit. Since the dispersion is independent of the mass of ion investigated, the instrument has special appeal for use in the heavy mass range. In ordinary deflection type instruments, such as those discussed earlier in this chapter, the absolute dispersion falls off directly with an increase of mass. In preliminary tests it has been shown that for Rb^{87} and Rb^{85} the mass difference is 2.000 AMU whereas for K^{41} and K^{39} the mass difference is 1.999 AMU.

The synchrometer.—Smith (29)[5] has constructed an instrument which, because of its superficial resemblence to the synchrotron, he has called a synchrometer. Figure 5 shows a schematic cross sectional view of the device. Ions produced by thermionic emission or electron impact of gas leave a source through a slit S_1. A magnetic field perpendicular to the figure deflects through an angle of 180° as in the conventional 180° magnetic mass spectrometer. They now enter a "pulser" which consists of a triple slit assembly. S_2 and S_4 are grounded whereas S_3 is connected to a generator of square voltage pulses. A group of ions of small length (ΔL) near S_3 is decelerated by the first pulse applied. The deceleration is sufficient to cause them to miss the source housing on subsequent revolutions. This group is now allowed to "coast" in the circular trajectory for n turns. After time nT, where T is the period of revolution, a second decelerating pulse is applied which reduces the radius of curvature sufficiently that the ions will enter slit S_5 of the detector. The latter consists of a magnetic electron multiplier. Mass differences are determined from the difference in time for synchronization.

In the first model constructed, the radius of orbit 2 was 5 in. and the magnetic induction had a value of 820 gauss. At a pressure of about 5×10^{-6} mm. Hg, ions of masses 18, 28, and 44 found in the residual gases were observed after 70, 40, and 25 rotations respectively between pairs of pulses. The corresponding values of the resolution were approximately 8, 5, and 3×10^3.

It appears quite practical to obtain a long path length, and hence a high resolution, with a reasonably sized apparatus. Electrostatic focusing should reduce the losses of ions due to spreading along the direction of the magnetic field. A new and larger instrument now being designed is expected to yield a precision of 10^6 or more.

With a mixture of O_2 and SO_2 in the apparatus Smith (30) measured the mass difference on the doublet $(O^{16})_2$—S^{32} and obtained the value 31.9823 ± 0.0010 for the atomic mass of S^{32}. In this investigation the particles made 40 turns in orbit 2, the time of flight in this orbit being 840 μsec. The mass found for S^{32} compares very favorably with other recent values.

Atomic mass ratios by microwave spectra.—During the past few years a number of determinations of isotopic mass ratios have been reported through the use of microwave spectroscopy. The precision obtained is comparable with the best mass spectroscopic values reported, and a number of discrepancies in mass spectrographically determined values have been revealed. For example, for the mass ratio C^{35}/C^{37} Aston (31) gives 0.9459806 ± 300, Okuda *et al.* (32) give 0.9459452 ± 65. From microwave spectroscopy Townes *et al.* (33), Gilbert *et al.* (34), and Townes & Shulman (35) report values of 0.9459801 ± 50, 0.9459775 ± 40 and 0.9459906 ± 120, respectively. These results suggest that the value computed from the data of Okuda and his coworkers must be in error.

[5] The writer is indebted to Dr. Smith for the information prior to publication

In a recent research Geschwind (36) *et al.* have measured transitions in isotopic molecules of OCSe. By assuming values for two of the Se isotopes, $Se^{76} = 75.9465$ and $Se^{80} = 79.9478$ (computed from Bohr-Wheeler formula), they were able to give the masses of other isotopes as follows: Se^{74}, 73.9481 ± 6; Se^{77}, 76.9482 ± 4; Se^{78}, 77.9465 ± 4; Se^{82}, 81.9500 ± 6. Incidental to the work it was shown that the abundance of Se^{79} was less than 1/10,000.

Abundance Measurements in 1950

New electrical measurements.—During 1950 five elements previously investigated only by the photographic method were studied by the more sensitive and accurate electrical method.

Hayden, Hess & Inghram (37) made a careful analysis of erbium and lutecium. Ions were emitted thermionically from the heated oxide of the elements and the analyzed ion currents measured with a vibrating reed electrometer. The mass spectrometer used a 60°, 6 in. magnetic analyzer. Table IV gives the percentage abundances found for the erbium isotopes together with previously reported values. Upper limits for percentage abundance of other isotopes were set as follows: 160 and 161, 0.0008; 163, 0.0009; 165, 0.003; 169, 0.008; 171, 0.005; 172, 0.0014.

In the case of lutecium (cassiopeium) Hayden *et al.* confirmed the presence of Lu^{176} and gave its abundance as 2.60 $\pm$ 0.03 per cent. Mattauch & Lichtblau (38), who discovered the isotope, gave the abundance as 2.5 per cent. The other isotope is Lu^{175}. Hayden *et al.* also set the following upper limits for the percentage abundances of other isotopes: 177 and 178, 0.006; 173 and 174, 0.008.

Leland (39) employed a mass spectrometer similar to that used by Hayden, Hess & Inghram except that it used an electron multiplier as a detector. He examined scandium, gadolinium, dysprosium, holmium, erbium, and ytterbium. In the case of gadolinium the abundance values agreed closely with those found by Hess (40) in 1948. His search for other isotopes led to somewhat lower upper limits of abundances. The percentages given were as follows: Gd^{149}, 0.001; Gd^{150}, 0.0005; Gd^{151}, 0.0003; Gd^{153}, 0.005; Gd^{159}, 0.002; Gd^{161}, 0.001; and Gd^{162}, 0.002.

For dysprosium, Leland found abundance values agreeing closely with those previously given by Inghram, Hayden & Hess (41). No search was made for other isotopes. In erbium, Leland found values agreeing closely with those given by Hayden, Hess & Inghram (see Table IV). His upper limits of abundance on other isotopes were not as low as those of Hayden *et al.* and hence are not given here. In ytterbium his isotope abundance ratios agreed very closely with those given in 1949 by Hayden, Hess & Inghram (42) and are not given here. His upper limits or percentage abundances of other possible isotopes were somewhat lower than those of Hayden, Hess & Inghram. They were: Yb^{166}, 0.001; Yb^{167}, 0.0005; Yb^{169}, 0.0005; Yb^{177}, 0.001; Yb^{178}, 0.0005.

In 1932 Aston (43) showed that scandium consisted of a single isotope of

mass 45, the upper limit of abundance for other possible isotopes being 3 per cent. Leland showed that if other isotopes existed their upper limit in percentage abundance would be as follows: Sc^{41}, 0.001; Sc^{42}, and Sc^{43}, 0.0002; Sc^{44}, 0.0005; Sc^{46}, 0.002; Sc^{47}, 0.01; Sc^{48} and Sc^{49}, 0.0002.

In holmium, Aston (44) found a single isotope, Ho^{165}. No upper limits were set for other isotopes. Leland showed that the percentage abundance of other isotopes could not exceed the following values: Ho^{161}, Ho^{162}, Ho^{163} and Ho^{164}, 0.04; Ho^{166}, Ho^{167}, and Ho^{168}, 0.001; Ho^{169}, 0.004.

Thulium was investigated by Aston (44) in 1934 and an isotope Tm^{169} was found. No upper limits were set for other isotopes. Lagergren & Kettner,[45] using Leland's instrument, investigated this element and gave the following upper limits for percentage abundances of other isotopes: (Tm^{162}, 0.001; Tm^{163}, Tm^{164}, and Tm^{165}, 0.002; Tm^{166}, Tm^{167}, and Tm^{168}, 0.02; Tm^{170}, 0.01; Tm^{171}, 0.002; Tm^{172}, 0.003; Tm^{173}, 0.002; Tm^{174}, 0.004; Tm^{175}, 0.04; Tm^{176}, 0.003.

TABLE IV

PERCENTAGE ABUNDANCE FOR ERBIUM ISOTOPES

Observer	162	164	166	167	168	170
Aston (83)*	0.25	2	35	24	29	10
Wahl (85)	0.1	1.5	32.9	24.4	26.9	14.2
Hayden Hess & Ingraham (37)	0.136 ±0.003	1.56 ±0.03	33.41 ±0.3	22.94 ±0.2	27.07 ±0.3	14.88 ±0.2
Leland (39)	0.154 ±0.007	1.60 ±0.02	33.36 ±0.3	22.82 ±0.2	27.02 ±0.3	15.04 ±0.2

* The 162 and 164 values were given by Dempster (84).

The completion of the above researches in 1950 left only fluorine, aluminum, yttrium, ruthenium, and thorium as naturally occurring elements uninvestigated by the electrical method.

Precision isotope abundance measurements.—In measuring the relative abundances of isotopes by mass spectroscopic methods, care must be taken to minimize sources of systematic error. In using a modern mass spectrometer the ion currents are steady and accidental errors are minimized. The electrical measurement of the ion currents with inverse feedback amplifiers and modern high resistance input resistors insures linearity of output signal with ion current intensity over enormous ion current ranges. While progress has been made in reducing errors caused by different response of some components of mass spectrometers to substances of different mass, this effect remains as perhaps the major source of error in isotope abundance measurements. In the analysis of gases the method of admitting the sample to the mass spectrometer vacuum may lead to a systematic error. The ion source

and mass analyzer may introduce other discriminatory errors. If the source of ions is thermionic, the nature of the emission phenomenon itself may discriminate against ions of different mass.

In the case of elements which can be introduced into the mass spectrometer as a gas or vapor, mass discriminating effects may be minimized by calibrating the instrument with very exactly determined synthetic isotopic mixtures made from separated isotopes. Nier (46, 47) has investigated 10 elements by this method. Argon standards were made by mixing nearly pure samples of A^{36} and A^{40}. The resultant A^{36}/A^{40} ratios were near 0.01 and were believed to be accurate within a few tenths of a per cent. The elements studied were common ones, readily available to any investigator. Thus interchecks between laboratories should be possible in the future.

For argon extracted from the atmosphere by absorbing the nitrogen and oxygen on hot lithium metal, Nier (46) gives the percentage abundances as 99.600 ± 0.002, 0.063 ± 0.001, 0.337 ± 0.001 for A^{40}, A^{38}, and A^{36} respectively. Earlier values given were: Vaughan, Williams, & Tate (48), 99.67, —. 0.33; Nier (49), 99.633, 0.060, 0.307; Dibeler, Mohler & Reese (50), 99.57, 0.08, 0.35.

In atmospheric nitrogen, Nier (46) finds $N^{14}/N^{15} = 273 \pm 1$. Earlier values appearing in the literature include: Urey & Murphy (51), 274.5; Vaughan, Williams & Tate (48), 265 ± 8; Wahl, Huffman & Hipple (52), 265.

For atmospheric oxygen, Nier (46) gives the percentage abundances as: O^{16}, 99.759 ± 0.005, O^{17}, 0.0374 ± 0.0003; O^{18}, 0.2039 ± 0.0003. The conversion factor between the physical and chemical atomic weight scale computed from these abundances is then 1.0002783 ± 0.0000005. However, the author warns that since the oxygen isotope ratios are known to be different in different sources of oxygen, the value might be as low as 1.000268. In brief this means that unless the source of oxygen with which a comparison is made is known, it is meaningless to give chemical atomic weights beyond one part in 100,000.

In carbon extracted from limestone, Nier (46) gives the percentage abundances as C^{12}, 98.892 ± 0.004, C^{13}, 1.108 ± 0.004, which agree closely with the earlier ones of Murphey & Nier (53). In potassium extracted from New Mexico Sylvite the percentage abundances found were: K^{39}, 93.08 ± 0.04; K^{40}, 0.0119 ± 0.0001; K^{41}, 6.91 ± 0.04. The K^{39}/K^{41} ratio agrees well with the recent value 13.66 ± 0.1 given by White & Cameron (54). The K^{40} value is about 10 per cent higher than previously thought to be the case (55, 56, 57). The higher value will affect the half life of K^{40} computed from β-ray counting measurements.

In neon widely varying abundance ratios have been reported. Nier's new values (47) together with previous results are given in Table V. In krypton, rubidium, xenon, and mercury, the values found agree well with earlier results [the reader is referred to reference (47) for detailed comparisons].

Variations in Isotope Abundance Ratios and Applications

The improvement of mass spectrographic and mass spectrometric techniques in recent years has placed the isotopic constitution of the naturally

occurring elements on a firm footing. The relative abundances of the isotopes of practically all elements are now very well known. The search for possible rare isotopes has been so thorough that few stable isotopes will be found in the future. However, the very techniques which have so greatly reduced the amount of work remaining in the field of measurement of so-called natural elements have opened up entirely new avenues of research employing stable isotopes or mass spectrometers. A number of examples of such new work in physics follows.

Nitrogen from radioactive minerals.—Yagoda & White (58) have examined the nitrogen found in old uranium and thorium minerals and found N^{15}/N^{14}

TABLE V

ISOTOPE ABUNDANCE RATIOS IN NEON

	Ne^{21}/Ne^{20}	Ne^{22}/Ne^{20}
Nier* (1950)	0.002827 ± 0.000006	0.09703 ± 0.0004
Dibeler *et al.*†	0.00309 ± 0.0002‡	0.1018 ± 0.002‡
Vaughan *et al.*§	0.0030	0.1081
Bleakney‖	0.0028¶	0.082¶
	0.0030**	0.092**
Hibbs††	0.0033 ± 0.0001	0.1080 ± 0.0001

* See reference (47).
† See reference (50).
‡ Maximum deviation.
§ See reference (48).
‖ See reference (86).
¶ For singly charged ions.
** For doubly charged ions.
†† See reference (87).

ratios 1.41 to 1.63 times greater than in nitrogen from the atmosphere or other common sources. There appears to be an "age" effect, the older minerals having the larger N^{15}/N^{14} ratios. The discovery of isotope abundance ratios differing so far from normal in an element where isotopes are presumably not formed by radioactive decay is extremely interesting. Further work to verify and if possible to extend these results is very much in order.

Nitrogen in the atmosphere.—McQueen (59) has examined the N^{15}/N^{14} ratio in air samples collected at various altitudes. He finds no variation up to 40 km. The ratio seems to fall, more or less regularly, as the altitude is further increased. In the range 55.4 to 58.8 km. the ratio is 3.9 ± 0.4 per cent lower than at ground level. The variations are believed due to settling in the earth's gravitational field. The measured variations are less than one would expect under idealized settling conditions. The difference is explained as due to stirring. Below 40 km. the mixing prevents any measurable separation.

Terrestrial and meteoric sulfur.—Macnamara & Thode (60) have measured the S^{32}/S^{34} abundance ratio in a large number of meteorites and compared the results with those found earlier (61) for terrestrial sulphur. In the case of the terrestrial samples the abundance ratio varied over a range of 5 per cent among the samples studied. For the meteoric samples no variations

in the ratio were observed although a change from normal of a few hundredths of a per cent could have been detected. The numerical value for the ratio lies about midway between the extremes found for the terrestrial samples. Macnamara & Thode suggest that meteoric and terrestrial sulfur had a common origin and whereas meteoric sulfur remained unaltered, that on the earth suffered alternations as a result of biological and geological processes.

Determination of fission product isotopes.—Several mass spectroscopic determinations of fission product isotopes have been reported. In 1947 Thode & Graham (62) reported on the stable isotopes of krypton and xenon observed from the decay of fission product chains in U^{235} fission. Inghram, Hess & Reynolds (63) in 1949 were able to determine the relative yields of several radioactive cesium isotopes by means of a mass spectrometric analysis and concluded that the fission yield curve was not a smooth one. In a careful examination of the xenon formed in the fission of U^{235}, Macnamara, Collins & Thode (64) concluded that the amount of Xe^{133} was 20 per cent higher than was predicted by a smooth fission yield curve. This work gives further evidence for "a fine-structure" in the fission yield curve. Because it was possible to make the isotope analyses a short time after the irradiation, the amount of Xe^{133} remaining was sufficient to measure its relative abundance over a period of time. The half life of 5.270 ± 0.002 days computed for the Xe^{133} is believed more accurate than that found from the more conventional radiochemical method.

In another research Macnamara & Thode (65) extracted the krypton and xenon from old pitchblende and in each of these elements discovered an excess of several isotopes which they attribute to the spontaneous fission of U^{238}. Although only 5×10^{-4} scc. of total krypton and xenon were extracted, complete isotope analyses were possible on both elements. In krypton, Kr^{83}, Kr^{84}, and Kr^{86}, and in xenon, Xe^{129}, Xe^{131}, Xe^{132}, Xe^{134}, and Xe^{136}, were identified as fission product isotopes. The ratios of fission product xenon to normal xenon and fission product krypton to normal krypton were 44:1 and 1:24, respectively. An interesting aspect of the work was the detection of Xe^{129} resulting from the fission product. By comparing its abundance with that of another stable isotope of xenon for pitchblende of various geological ages it is hoped that a more accurate half life for I^{129} will be found than the value 10^8 years now assumed.

Xenon in tellurium minerals.—Inghram & Reynolds (66) have measured the amount and isotopic composition of the xenon found in old tellurium minerals. They find excess Xe^{129}, Xe^{130}, Xe^{131}, Xe^{134}, and Xe^{136}. The Xe^{129} and Xe^{131} are ascribed to the occurrence of (n, γ) reactions with Te^{128} and Te^{130} although some of the Xe^{129} may be the decay product of long life I^{129}, possibly present as an impurity. The excess Xe^{130} is attributed to a double-β decay of Te^{130}. From the measurements, the half life of this process is given as of the order of 10^{21} years. This value is to be compared with 6×10^{14} and 10^{24} years computed from the Majorana and Dirac theories of the neutrino respectively.

Stable isotopes as tracers to determine branching ratio in radioactivity.—

An ingeneous use of separated stable isotopes has been made by Reynolds (67). There are 62 known even-even isobaric pairs which differ in atomic number by two and are separated by an unstable odd-odd nucleus of the intermediate atomic number. According to β-decay theories the intermediate nucleus should be unstable with respect to both isobaric transitions $Z \rightarrow Z-1$ and $Z \rightarrow Z+1$. Branching has been observed in 12 of the 62 cases. Reynolds studied the decay products found from the disintegration of Cu^{64}, Br^{80}, Br^{82}, and I^{128}. These isotopes were made by (n, γ) reactions in prolonged irradiation of the elements in a graphite moderated uranium pile.

In the case of copper, the procedure was to dissolve the irradiated copper and to add known amounts of stable Ni^{68} and Zn^{68} to the solution. An isotopic analysis of the zinc and of the nickel in the solution was next made. From the relative abundances of the isotopes in each of the two elements, it was possible to determine the amounts of Ni^{64} and Zn^{64} formed as a result of the disintegration. The method eliminates the need for a quantitative recovery of the zinc and nickel from the solution and hence is capable of high accuracy.

In the case of the other nuclei studied the procedure was similar. The final results given are:

$$\lambda_{\pm}(Cu^{64}) = \text{radiogenic } Ni^{64}/\text{radiogenic } Zn^{64} = 1.62 \pm 0.11$$
$$\lambda_{\pm}(Br^{80}) = \text{radiogenic } Se^{80}/\text{radiogenic } Kr^{80} = 0.090 \pm 0.002$$
$$\lambda_{\pm}(Br^{82}) = \text{radiogenic } Se^{82}/\text{radiogenic } Kr^{82} < 0.00027$$
$$\lambda_{\pm}(I^{128}) = \text{radiogenic } Te^{128}/\text{radiogenic } Xe^{128} = 0.053 \pm 0.002.$$

The method is especially effective in detecting orbital electron capture. Previous methods used depend upon measuring secondary effects such as nuclear γ rays, x-rays, or Auger electrons. However, it may not be applied without some knowledge of the decay system since it will not distinguish between orbital electron capture and positron emission or isomeric activities having different decay periods unless one of the activities is very long.

An extremely interesting application of the method has been made by Inghram *et al.* (68). K^{40} is known to decay to Ca^{40} by β-emission and A^{40} by K-capture. The exact value of the branching ratio has been a matterof some uncertainty, the literature containing very widely divergent values. Inghram and his co-workers determined the ratio of A^{40}/Ca^{40} in a 10^8-year-old KCl sample of Strassfurt sylvite. A known amount of separated A^{36} was added to the gas extracted from a known amount of sample; a known amount of separated Ca^{48} was added to a known amount of mineral which had been put into solution. From isotopic analyses of the argon and calcium, the radiogenic A^{40} and Ca^{40} content of the mineral are found without the necessity of making a quantitative extraction of the argon or calcium from the mineral. The ratio $\gamma_K/_\beta$ computed from the data is given as 0.126 ± 4 per cent. Because of the possible loss of argon from the mineral this is taken as a lower limit. The agreement of this ratio with the value 0.135 ± 0.04 given by Sawyer & Wiedenbeck (69) from direct counting experiments is gratifying.

Isotopic composition of argon found in potassium minerals.—Smits & Gentner (70) and Pahl *et al.* (71) have made a careful determination of the argon found in several potassium minerals. Whereas the samples studied by Aldrich & Nier (72) in 1948 sere found to contain an appreciable amount of atmospheric as well as radiogenic argon, the argon observed in a number of the samples studied in the new work was essentially pure A^{40}.

The age of a sample of Buggingen sylvine is computed to be 20 million years and that of sylvine from Friedrichshall 200 million years. In computing the age of the sylvine samples studied from the radiogenic A^{40}/K^{40} ratio found in the mineral, the authors assumed that there were 3.0 $K^{40} \rightarrow A^{40}$ disintegrations per gm. potassium per sec. The new work of Inghram *et al.* (68) and Sawyer & Wiedenbeck (69), already mentioned, indicates that the 3.0 is too small and should be replaced by 3.6 or more. This would reduce the age computed somewhat. Nevertheless it is clear that the decay constants and branch ing ratio are now known sufficiently well to make worthwhile more studies like those of Gentner and his colleagues in order to fully explore the possibility of measuring geological age by the $K^{40} \rightarrow A^{40}$ or $K^{40} \rightarrow Ca^{40}$ method.

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HIGH ENERGY ACCELERATORS

STANDARD CYCLOTRON[1]

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The standard or fixed frequency cyclotron is limited in energy by the relativistic increase of particle mass, but has the advantage of high beam intensities available because of continuous operation. The practical energy limit is about 20 million electron volts for deuterons (or 40 M.e.v. for He^{++} ions), set by the economics of cost versus output rather than the absolute physical limits. Energies achieved with most of the larger cyclotrons are sufficient to penetrate potential barriers of even the heaviest nuclei, so that total cross sections for nuclear reactions approach the geometrical cross sections of target nuclei. This high disintegration probability and the high beam intensities result in large yields of neutrons or induced radioactivities, and define the chief field of usefulness of the standard cyclotron.

The cyclotron is second only to the atomic pile as a source of induced radioactivity, and even in this field has a special sphere of usefulness in production of certain types of activity not available through neutron reactions in the atomic pile, such as positron activities following (d, n), $(n, 2n)$ and (α, n) reactions. Although it cannot compete with the pile as a source of thermal neutrons, it can produce neutrons of much higher maximum energy (10 to 20 M.e.v.) which are useful in a variety of other experiments and processes. And pulsed operation of the cyclotron allows microsecond timing of neutron production, a feature not readily available with the pile.

Many scientists thought that the atomic pile would make the cyclotron obsolete, or at least restrict its usefulness. However, the past few years have shown a new burst of activity in the cyclotron field. Commercial firms have entered the design and construction field, and they have added to the instrument many features from engineering experience which should improve output and reliability. The Collins Radio Company has completed a 60-in. cyclotron for the Brookhaven National Laboratory, with a minimum specified performance of 20 M.e.v. deuterons; a duplicate machine is under construction for the Argonne National Laboratory. The General Electric Company has independently designed and has under construction a 60-in. machine of similar ratings for the National Advisory Committee for Aeronautics laboratory at Cleveland. Cyclotrons are completed or under construction in many foreign laboratories. An 85.5-in. magnet at the Nobel Institute in Stockholm has been completed as a standard cyclotron and is now operating at 20 M.e.v. deuterons; an 86-in. magnet at the Oak Ridge National Laboratory produces 20 M.e.v. protons; these are the largest standard cyclotrons

[1] This review is essentially a survey of papers published in 1950.

in point of size. A recent survey of particle accelerators (1) lists 14 cyclotrons in Europe and England and 21 in the United States. Practically all of these machines are in scientific laboratories, supporting research in nuclear physics or producing tracer radioactivities for research in chemistry, biology, and medicine.

In a review of this type it seems unnecessary to repeat the descriptions of physical principles and basic designs available in earlier publications. It is assumed that the reader is acquainted with these principles. If not, review articles (2, 3) are available to give a familiarity with the general features of the cyclotron. It is proper, however, to give due credit to Professor Ernest O. Lawrence of the University of California, who first conceived the cyclotron, and who has been the inspired leader of the Berkeley laboratory where a large share of the early development of the cyclotron took place. The Berkeley 60-in. machine was the first of the big cyclotrons and set the pattern for others of this size. The group at Berkeley comprised many competent engineers as well as scientists, and they early visualized the importance of utilizing all possible technical aids. Other laboratories have joined in the engineering development, notably the Massachusetts Institute of Technology; and each group has made some contribution to cyclotron design or technique. The modern cyclotron is the sum of all such contributions and experience.

Technical Improvements

The continued development of the cyclotron as a source of supply of neutrons and radioactivities has resulted in a variety of improvements in design and technique during recent years, aimed at increasing output and achieving more stable, reliable operation. They consist principally of developments taking advantage of engineering experience and utilizing modern equipment and materials. Such developments have proceeded on each of the major components of the cyclotron. They can be described briefly in words, but details can be found only in the stacks of design blueprints or circuit diagrams, or by close inspection of the modern cyclotrons.

Machined forgings of mild steel have largely displaced castings or laminated construction for magnetic circuits. This is the result of improvements in technique in steel mills so that large forgings can be produced economically. Such forgings can be readily machined to give the precise dimensions required in the pole gap. A minimum of pieces are used, usually consisting of six: two poles, two uprights, and two yokes. Steel companies have taken this problem from the physicists and have done a workmanlike job of engineering the magnetic circuit. The magnetic properties of mild steels have improved with experience and now approach the best of "soft" irons.

Heavy mechanical construction having lots of water tubes or channels for cooling is to be noted in chamber and electrode designs. Large coaxial quarter-wave resonant lines (or the equivalent shielded-pair line), with the resultant high electrical efficiency and mechanical rigidity, are in general use for the electrical circuit used to generate the high potentials required for the electrodes or "D's." Such lines are part of the chamber vacuum system so the resonant circuit is vacuum-insulated; insulating supports for the elec-

trodes have been abandoned. Oscillator circuits utilize high power television transmitter tubes (such as the 880) which are close-coupled to the resonant lines, usually mounted directly over the lines .The most common design is a push-pull circuit using pairs of the tubes, drawing excitation from the resonant lines; others have found advantages in external excitation from a frequency-controlled master oscillator. Power supplies use a maximum of commercial equipment such as rectifiers, constant current networks, and voltage regulators.

Vacuum techniques have undergone a steady development toward larger and faster pumps, simpler and more reliable seals, and more sensitive gauges and leak detectors. The primary problem of high intensity cyclotron operation is control of the gaseous discharges which occur in the chamber and which liberate large quantities of gas from the metal electrodes and walls. Such a discharge tends to maintain itself as a high-pressure low-voltage arc, and it is seldom possible to "condition" a metal chamber simply by maintaining this continuous discharge. Fast pumps are essential to evacuate the gases released in the discharge at a rate sufficient to keep the pressure in the chamver below the threshold pressure for maintaining the low-voltage arc. A pumping speed of at least 10,000 l. per sec. (measured at 10^{-5} mm. of Hg pressure) is considered necessary for a 60-in. cyclotron chamber; this requires a pump of the order of "30-in." diameter and correspondingly large pumping apertures and baffles. Vacuum seals have become more or less standardized with experience. The basic pattern is a narrow rubber gasket confined in a groove and compressed to give metal-to-metal contact between flanges. The commercially available "O-Rings," which have a round cross section and are made in a wide range of sizes, have been adapted to this use in many laboratories. Finally, the use of the helium mass-spectrographic leak detector, now developed to be a reliable laboratory test instrument, has largely solved the problem of leak hunting in large metal vacuum systems.

Cyclotron scientists have become increasingly aware of the importance of accurately uniform magnetic fields, with the proper radial decrease needed for focussing. Instruments and techniques for measurement of magnetic field have had a steady development, so it is now possible to observe variations as small as 0.1 per cent with precision. Cyclotron ions can have "betatron" type free oscillations in both the radial and vertical directions superimposed on the expanding equilibrium orbit; such oscillations can cause ions to strike the D's during acceleration, or the deflecting channel during ejection. It is now clear that azimuthal inhomogeneities in the field can set up large amplitude radial oscillations and result in serious loss of intensity. An estimate of the azimuthal homogeneity required for minimum loss of intensity has been obtained at Massachusetts Institute of Technology after a careful program of measurement and correction; the allowable variation in field is found to be in the order of 0.2 per cent for all radii out to the exit position. The modern method of magnetic field correction is to measure and eliminate inhomogeneities previous to operation, rather than to depend on the cut-and-try techniques of empirical shimming during operation used in the past.

Radiation protection for personnel has become a serious problem with high intensity cyclotrons. Two phases of this problem are of about equal importance. The first is the danger from radiations given off during operation, primarily fast neutrons. This problem has been underlined by the recent discovery of cataract damage in the eyes of some 10 or 12 cyclotron personnel. The first step in solving this problem was to note the danger of careless techniques used in early days such as looking into the viewing window with the cyclotron operating, and to eliminate such risks by thorough publication of the danger. The remaining step is that of installing adequate shielding of the cyclotron when in operation. The other phase of the radiation hazard is exposure to β- and γ-rays from induced radioactivities incurred during target changing, maintenance, or repair operations. This becomes a matter of good housekeeping, use of remote-handling techniques wherever possible, use of local shielding during manipulations, and continuous vigilance in keeping the duration of exposure a minimum.

The completely closed vault with a minimum of apertures has become standard design for cyclotron laboratories. Movable doors with overlapping side panels have displaced the labyrinth entry used in early designs; a baffled entry through the shielding walls must be long and tortuous to result in as efficient shielding as a solid door. Water tanks have been completely displaced, in favor of solid construction. The most satisfactory material in use is concrete loaded with iron ore or scrap iron to increase density for γ-ray absorption and at the same time provide material with large cross section for inelastic scattering of neutrons. Typical of recent designs is the vault for the Brookhaven 60-in. cyclotron. This vault has 5-ft. walls and a 4-ft. roof of limonite-loaded concrete; two 5-ft. thick concrete doors are raised or lowered into pits below floor level by electric motor drive, one of 8 by 8 ft. for large apparatus and one 3 by 7 ft. for personnel access. Ports are provided for handling radioactive targets through the walls and for bringing an emergent beam through into an auxiliary vault for experiments. This amount of shielding will reduce fast neutron intensity, by a factor of about 10^{-5}, and slow neutrons or γ-rays by about 10^{-6}. To keep leakage through apertures down to an equivalent small fraction of incident intensity, the area of such apertures is kept less than 10^{-5} of the total area, and apertures are designed to eliminate direct radiation leakage. Conduits for ventilation or electrical leads have double bends, and doors are overlapped to prevent straight channels through the shield.

Safe handling of radioactive materials is now a well-known technique, highly developed in the several pile laboratories. Cyclotrons which produce dangerous quantities of activities have usually been equipped with small "hot labs" based on such pile experience. But target handling techniques used in preparing targets for the hot lab have not been as well perfected, although some progress has been made. A small shielded machine has been developed at the Massachusetts Institute of Technology to mill the face off metal block targets after bombardment. In general, however, the use of quick-acting valves and gates and handling with tongs is the accepted method of reducing exposure. Personnel exposure to radioactivity in and about the

cyclotron target region during target removal is usually more serious than exposure from the target itself during this handling. So some thought has been applied to remote controlled target handling devices, so that targets can be changed without personnel exposure. Up to the present none of these systems has had a practical test in operations.

Major repairs to the cyclotron involving removing the D's or substituting new parts also endanger the maintenance personnel. The only practical technique at present is to reduce exposure to a minimum by careful handling and local shielding, and to keep individual doses below the critical level by rotation of personnel. Continued engineering development to reduce frequency of breakdowns has kept this problem under control, but has not resulted in a permanent solution. It is an unfortunate fact that cyclotron maintenence personnel are still occasionally exposed to a serious radiation hazard in many laboratories; only the greatest care in measurement of dosage and rotation of personnel receiving the exposures will avoid serious injury.

Instrumentation for Research

Another area of development in the cyclotron field is the instrumentation for research utilizing the primary radiations, as distinguished from the development of the cyclotron as a production source of activities. Beams of neutrons from the cyclotron target can themselves be used for nuclear studies. And the emergent beam of high energy deuterons, protons, or alpha particles can be used to study the primary disintegration processes. The intense background of mixed radiations from a cyclotron, combined with the angular and energy spread of the emergent beam, has tended to limit the use of the machine for direct studies of reactions. However, several laboratories have tackled and overcome the difficulties and are putting the cyclotron to good use as a research instrument.

In order to utilize the emergent beam, an auxiliary magnet is used to analyze and focus the ions so that they can be piped through a shielding wall to a region of lower radiation intensity where experiments can be performed. This has been accomplished at Los Alamos (4), at the University of Pittsburgh, and at the Massachusetts Institute of Technology (5), with equivalent results. The method used at Los Alamos is to send the divergeng beam through a trapezoid-shaped magnetic field which brings the beam through a pipe in a 4-ft. shielding wall to an approximate focus about 10 ft. beyond the magnet. At the Massachusetts Institute of Technology, a magnet with tilted pole faces is used to accomplish the same result. Focussed beams of the order of 1 μ amp. are obtained in this way. Background intensities are still large, particularly if the beam must be further defined by slits, but are many orders of magnitude smaller than near the cyclotron itself.

Detection instruments used with cyclotrons must be capable of observing the desired particles in an intense background of other radiations. A basic technique is the use of multiple time coincidence. Triple- and quadruple-coincidence counter telescopes have been developed at Los Alamos, at Pittsburgh, and at other laboratories to observe protons recoiling from high energy neutrons, or protons from a bombarded target. Such a counter tele-

scope is pointed at the target and multiple time-coincidences can readily be observed above the background of random coincidences due to background radiation. An even more special instrument has been developed at the Massachusetts Institute of Technology (5) for the selective detection of different charged particles from a target. This instrument, known as a "triple proportional gated coincidence counter" adds the feature of pulse height discrimination to that of time coincidence. Pulses proportional to the ionization in each of three shallow chambers along the track of the particle are sent through discriminator circuits to pick out only those pulses which are representative of a single species of particle; time coincidences between these gated pulses identify the type and energy of the particle. Protons, deuterons, tritons, and alpha-particles can be distinguished and their energy measured.

Pulsed operation of the cyclotron has been used in conjunction with time-gated counters to detect neutrons of a particular velocity. The principle invoked is to generate a short burst of neutrons at the target using a pulse of accelerated ions from the cyclotron, and then to observe neutrons at a considerable distance from the target after various time delays. High energy neutrons will arrive at the counters in short times, and slow neutrons after a longer time. If the counters are made sensitive only for a short time interval which can be delayed after the ion pulse by a known time, they will respond only to neutrons of a narrow velocity range. Such "time-of-flight" instruments have been perfected in several laboratories, notably at Cornell and at Columbia University (6), in which the circuits for pulsing the cyclotron beam and for timing the neutron counters have been highly developed. Neutrons with energies between 0.01 and 10,000 e.v. have been used to study neutron absorption and scattering in many elements as a function of neutron energy. Neutron resonances have been observed in many elements and absolute cross sections have been obtained. The value of this technique for the study of neutron properties can hardly be overestimated.

Another use for pulsed operation of the cyclotron is in the study of extremely short period radioactivities. Counters placed near the target can be used to measure the intensity of radioactive decay as a function of time after the end of a short pulse. Radioactive periods of 1 sec. or less have been observed, and the technique has been used to search for periods in the millisecond range.

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HIGH ENERGY ACCELERATORS

SYNCHROCYCLOTRON[1]

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The relativistic limitation on energy for the fixed-frequency cyclotron has restricted the size of magnets to the order of 60-inch pole face. This limitation can be removed, larger magnets can be utilized and the ions can be accelerated indefinitely by modulation of the applied frequency to match exactly the ion rotation frequency. The relativistic relation between ion rotation frequency and ion energy can be expressed as:

$$f = \frac{eB}{2\pi m} = \frac{c^2 eB}{2\pi(E_0 + T)}$$

where E_0 is the rest energy and T the kinetic energy of an ion of charge e in mass m in a magnetic field B, and c is the velocity of light. Both the increasing kinetic energy and the radially decreasing magnetic field required for focusing result in a decrease in ion rotation frequency with increasing particle energy. To keep in resonance with the particles the applied frequency must be decreased; this amounts to a 30 per cent decrease for protons of 400 M.e.v. if the magnetic field is assumed to drop by 5 per cent in the process.

The use of frequency modulation as a remedy for the relativistic limitations of the cyclotron was suggested by McMillan (1) in 1945 as one of the possible applications of the principle of phase stable synchronous acceleration. McMillan, and independently, Veksler (2) in the USSR, pointed out that particle orbits in a cyclotron-like magnetic field and accelerating gap would be stable and that, if disturbed, the particles would perform oscillations in phase of crossing the accelerating gap. Associated with the phase oscillations are oscillations in energy and in radial position about an equilibrium orbit. Furthermore, each equilibrium orbit is associated with a particular particle energy for a given magnetic field and has a specific frequency of revolution. If either the magnetic field is increased or the applied frequency decreased slowly, the particles will follow this change adiabatically by a shift in phase of crossing the accelerating gap so as to gain energy slowly and remain in resonance. The first method, of increasing magnetic field, is utilized in the electron synchrotron; the second method, of frequency modulation, is adapted to the acceleration of heavy particles in the synchrocyclotron. While accelerating, the particles oscillate in phase of crossing the accelerating gap, acquiring just sufficient energy on the average to maintain an expanding, equilibrium orbit which is in resonance with the applied frequency. As a con-

[1] This review is essentially a survey of papers published in 1950.

sequence, the particles are bunched in phase and energy, and one such bunch of ions is accelerated to high energy in each frequency sweep. The frequency is modulated cyclically, resulting in a sequence of pulses of high energy ions at the modulation rate. A more complete description of phase focusing and particle bunching is given in a recent survey article on synchronous accelerators (3).

The pulsed character of the output of a synchrocyclotron results in a lower duty cycle and lower average beam current than with the standard cyclotron. On the other hand, particle energy is limited only by the size of magnet and intensity of the magnetic field. The maximum proton energy obtained to date is 385 M.e.v., with the Columbia machine. For any energy above about 200 M.e.v., protons are capable of creating mesons in nuclear interactions; so one of the most important fields of research opened up by the development of the synchrocyclotron is the study of meson production processes and the properties of mesons. Other machines, which have been designed for energies below the meson threshold, are intended to study the details of high energy nuclear processes such as the scattering of protons and neutrons, the production of induced radioactivity and the complicated nuclear reactions observed at high bombarding energy. So the synchrocyclotron has found its field of usefulness as a research tool for high energy nuclear physics, leaving to the standard cyclotron the field of production of neutrons and induced radioactivities.

Listing of Synchrocyclotrons

The first test of the principle of the synchrocyclotron was made at the University of California (4), using the 37-in. cyclotron magnet, by an ingenious method of simulating the expected relativistic mass change with an exaggerated radial decrease in the magnetic field. The success of this model led to the modification of the 184-in. magnet which was originally intended to be a standard cyclotron of large size. It was completed in November, 1946, designed originally to produce deuterons of 200 M.e.v. or He^{++} ions of 400 M.e.v.; later it was converted to accelerate protons to 350 M.e.v.

The immediate success and the relative simplicity of operation of the synchrocyclotron has impressed all observers with the practicality of this principle, and stimulated many other laboratories to build similar ones. There are now four large machines in operation and two under construction in the United States; in several laboratories this rapid development was aided by Government funds made available through the Office of Naval Research. There are three synchrocyclotrons in operation in other countries and two more under construction. In preparing this review the author circulated a questionnaire to each of these laboratories; a summary of the replies is given in Table I.

In addition to the large machines listed in Table I, two laboratories, Princeton University and the University of California at Los Angeles, have converted small cyclotrons to the synchro-principle to achieve higher energy

protons (17 M.e.v.) than available with a standard cyclotron. Another installation deserving special mention is the "cyclosynchrotron" under construction by M. L. Oliphant (5) at the Australian National University in Canberra. This instrument will have a synchrocyclotron of 136-in. diameter

TABLE I

STATUS OF SYNCHROCYCLOTRONS IN THE UNITED STATES AND EUROPE

Synchrocyclotrons in Operation

Location and (Supervisor):	Pole Diam.: (in.)	Particle-Energy: (M.e.v.)	Magnet Weight: (tons)	Magnetic Field: (kg.)	Pulse Rate: (c/s)	Av. Beam Current: (μa)	Approx. Cost: (excl. bldg.)	Date First Operation:
(United States)								
1. Univ. of Calif. (E. O. Lawrence)	184	p—350 d—200 α—400	4,300	15.0	60	0.75	—	Nov. 1946
2. Univ. of Rochester (S. W. Barnes)	130	p—240	1,000	17.0	100	0.1	—	Dec. 1948
3. Harvard Univ. (R. B. Holt)	95	p—130	700	16.5	50–200	0.1	$750,000	May 1949
4. Columbia Univ. (J. R. Dunning and E. J. Booth)	164	p—385	2,400	17.4	30–100	0.1	—	Mar. 1950
(Foreign)								
5. Amsterdam, Holland (C. J. Bakker)	71	d— 28	210	13.7	2,000	25.0	—	Sept. 1949
6. Harwell, England (T. G. Pickavance)	110	p—175	670	16.8	100	1–2	£300,000	Dec. 1949
7. McGill Univ. (J. S. Foster)	82	p—100	260	16.4	200	0.2	$200,000	June 1950
Synchrocyclotrons under Construction								
(United States)								
8. Univ. of Chicago (H. L. Anderson)	170	(p—450)	2,200	18.6	50–360	—	$2,500,000	—
9. Carnegie Inst. Tech. (E. C. Creutz)	141.7	(p—440)	1,500	20.5	300	—	$2,000,000	—
(Foreign)								
10. Upsala, Sweden (The Swedberg)	90.5	(p—200)	720	22.0	500	—	3 M Sw. Kr.	—
11. Univ. of Liverpool (H. W. B. Skinner)	156	(p—400)	1,640	18.0	—	—	—	—

producing 200 M.e.v. protons as an ion source for a 2,000 M.e.v. proton synchrotron.

TECHNICAL FEATURES

The technical problems of design and construction for the synchrocyclotron are in most instances, except for size, the same as for the standard cyclotron. The larger magnet, vacuum chamber, accelerating electrode, power supplies, etc., are mostly straightforward engineering extensions of cyclotron designs. Adequate descriptive detail is available in the progress reports from several laboratories (6, 7, 8). In a few cases, the problems of the

synchrocyclotron are different. For example, the radiofrequency power supply for the accelerating electrode must be modulated cyclically. This is accomplished by having a rotating variable capacitor electrically connected to the electrode, modulating the resonant frequency of the electrode circuit which is driven by a self-excited oscillator. Oscillator power requirements, on the other hand, are much smaller than for the standard cyclotron, since the ions make many more revolutions and require less voltage per turn; 10 to 20 kv. peak potential on the single "D" is adequate for most machines. Considerable variety has shown up in designs for the rotating capacitor, but all of them have proven satisfactory in service.

Certain laboratories claim special valuable features in design. The University of California has pioneered in basic designs, in the development of ejection techniques, and in methods for utilizing the internal beam. The Carnegie Institute of Technology has developed a shimming technique which allows use of 96.5 per cent of the pole face radius. The University of Chicago has carried magnetic measurements and shimming to a high stage of perfection, in order to reduce amplitudes of undesirable radial and vertical oscillations, and has also developed a new technique for ejecting an emergent beam. Columbia University has the rotating capacitor located along the diametral face of the "D" circuit, thereby avoiding large external structures. At Amsterdam, a new type ion source has resulted in unusually high beam intensity.

The ejection of an emergent beam from the synchrocyclotron is extremely useful for physical experiments, even though ingenuity in devising experiments with the resonant beam within the chamber has been notable in many laboratories. Ejection is possible with varying efficiency using several different principles. It seems probable that the most efficient system has not yet been conceived. The systems which have been proposed and in some instances tested in operations are the following (8):

(*a*) *Nuclear scattering deflector.*—A high Z probe is placed in the cyclotron at the desired radial position and protons are scattered through relatively large angles, sufficient to have some of them enter the mouth of a magnetic shielding channel in which the cyclotron magnetic field is weakened sufficiently to allow the protons to pass out of the field on an opening spiral path. The efficiency of this device, which has been used for some experiments at Berkeley and at Harwell, is less than 0.1 per cent.

(*b*) *Electrostatic pulse deflector.*—A long electrostatic field between curved electrodes (extending over a quadrant or more of the particle orbit at the periphery) is pulsed to exert a radial field on the ions passing through the field. The ions are shocked into radial oscillations and when they reach maximum outward amplitude enter the mouth of a magnetic shielding channel. The required electric field is very high, approaching break-down limits, to provide sufficient deflection for high energy ions, and should be applied in a time short compared with the time for an ion revolution ($<0.1\ \mu$ sec.). At Berkeley this system has been very successful; about 10 per cent of the protons enter the magnetic channel and of those entering the channel about 2 per

cent are available in an external beam at some distance from the cyclotron. A deflector using the same principle has been designed at Harwell, but not yet tested.

(*c*) *Axial deflector.*—The combination of a vertical electrostatic field and a magnetic shielding channel located above or below the median plane offers a convenient geometry and is economical in pulse power. It has not been worked out in detail, but should give an efficiency equivalent to the radial electrostatic pulse deflector.

(*d*) *Magnetic peeler.*—A magnetic shield shaped to weaken the magnetic field over a short arc near the periphery will set up radial ion oscillations. Under certain conditions, for a narrow range of values of "n" (the exponent defining the radial decrease in field), these oscillations will grow in magnitude until some ions fly out into open orbits. This device, called a "peeler," has been used to extract small intensity emergent beams of electrons from the betatron at the University of Illinois.

(*e*) *Regeneration deflector.*—At the University of Chicago a detailed design study has been made of an extension of the peeler principle consisting of two magnetic inhomogeneities. In this scheme a peeler which weakens the field at one azimuth sets up radial oscillations having a maximum outward amplitude approximately one quadrant later; because of the small but finite value of "n" (<0.2), the ions will not have completed a radial oscillation when they again reach the peeler, and so will pass inside it if this is the only discontinuity. A second magnetic discontinuity called a "regenerator" located 90° beyond the peeler strengthens the field locally and overcompensates the effect of the peeler; ions traversing both discontinuities pass through the peeler at a larger radius than in the first traversal and so the effect is regenerative, building up radial amplitudes until the ions can be directed into a shielding channel. This system has promise of giving higher efficiency than the electrostatic deflector, but has not yet been tested in operation.

The shielding requirements for a synchrocyclotron do not differ in principle from those for the standard cyclotron. The higher energy radiations do require greater thickness of shield for attenuation; on the other hand, the lower duty cycle and the correspondingly lower average beam make the scattered radiation intensity much smaller. As a consequence the shield must be thicker in the horizontal plane of the primary, high energy radiations, but can have a thinner roof. This has been carried to an extreme at the University of Rochester, where there is no overhead shielding, and it is admitted to result in undesirably high intensities of scattered radiation. A structure of overlapping concrete blocks is used at Berkeley, forming a wall 15 ft. thick and with a 4-ft. layer overhead. A completely closed vault with movable doors 8 ft. thick is the answer at Harvard. At Harwell and at the University of Chicago the cyclotron is located in a pit below ground level with heavy overhead concrete slab shielding. A useful contribution at this time would be a careful study of the shielding problem by one or more of the laboratories which have instruments in operation; at present information is incomplete

on the attenuation of high energy radiations, the intensity of scattered radiation and the effect of cracks or apertures in shields.

Experimental Results

The research output from synchrocyclotron laboratories during their short period of productivity has been phenomenal. The list of publications from the Berkeley group alone numbers over 100, and includes important papers on such topics as: meson production and detection, angular distribution of high energy neutron scattering, mass measurements for π- and μ-mesons, discovery of neutral mesons.

Machines designed for energies below the meson threshold have also been active in such fields as: proton-proton scattering at 100 M.e.v., neutron energy distribution in Be(p,n) reactions, total cross sections of H and C for high energy neutrons, excitation function for $C^{12}(p,3p3n)Be^{7}$.

The full critical analysis of these experimental results is covered elsewhere in this volume. It is clear, however, that the information they present of an energy range 10 times higher than previously available is of great significance. Each of the laboratories has an ambitious program planned for the future, and other important results are certain to be forthcoming.

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HIGH ENERGY ACCELERATORS

PROTON SYNCHROTRON[1]

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The proton synchrotron can produce the highest energies of any of the super-voltage accelerators, well above 1 B.e.v. Its purpose is to study the high energy nuclear processes of the cosmic ray energy range. The instrument is an extension of the synchrotron principle of phase stable acceleration at constant orbit radius in an annular magnetic field which increases with time, as for the electron synchrotron.

Magnetic accelerators for electrons, such as the betatron or the synchrotron, have a practical energy limit of the order of 0.5 and 1.0 B.e.v., respectively, as a result of the rapid onset of radiation losses by the orbiting electrons. This energy loss varies with the fourth power of the ratio of total energy to rest energy of the accelerated particle. Because of their larger mass, protons will not experience this limitation until much higher energies are reached. Furthermore the synchrocyclotron, which has been so successful as a proton accelerator in the 100 to 400 M.e.v. range, requires a solid core magnet; at several billion volts the magnet becomes exorbitant in weight and cost. Therefore, a ring magnet, accelerating protons by means of the synchrotron principle, seems to offer the most practical method of attaining such superenergies.

The synchrotron principle of magnetic particle acceleration arose from three independent sources at about the same time, another illustration of the parallelism of scientific development throughout the world. The first proposal of a proton accelerator was made by Oliphant of the University of Birmingham to the British Directorate of Atomic Energy in 1943; the details were not published until 1947 (1, 2). Meanwhile McMillan (3) at the University of California and Veksler (4) in the U.S.S.R. published papers in 1945 describing the principle.

Four proton synchrotrons are under construction. The first one to be started is at the University of Birmingham (1), designed for 1.3 B.e.v.; it has reached the assembly stage and may be ready to be tested within a year. The "Cosmotron" at the Brookhaven National Laboratory (5), designed for 3 B.e.v., is also in the final stages of assembly, and may also be ready for operational tests within a year. The "Bevatron" at the University of California (6, 7) has the highest energy expectations, of 6 B.e.v. ultimately; the process of magnet assembly is now underway. A fourth instrument, at the

[1] This review is essentially a survey of papers published in 1950.

Australian National University at Canberra (8), is in the early stages of design and construction; the goal is 2 B.e.v. and it is to utilize a 200 M.e.v. synchrocyclotron for initial acceleration, hence the name "cyclo-synchrotron."

The Acceleration Principle

The principle of operation is basically the same as for the electron synchrotron. A constant orbit radius is used with a ring-shaped magnet to produce a magnetic field normal to the doughnut-shaped vacuum chamber enclosing the orbit. Electrons approach their limiting velocity at about 2 M.e.v. energy (0.98 c, where c is the velocity of light); protons on the other hand do not reach the equivalent limit until they have acquired 4 B.e.v. energy. So the rotation frequency for protons at constant orbit radius, and hence the frequency of the applied accelerating electric field, will increase by a large factor during acceleration. This requirement of a variable frequency accelerating field is the only significant difference, except for size, between the proton and electron synchrotrons.

Ions are injected into the synchrotron orbit at low energy when the magnetic field is small and are accelerated by an oscillating electric field in resonance with the motion of the ions while the magnetic field increases to its maximum. If the applied frequency is correct, the ions oscillate in phase of crossing the accelerating gap, about an equilibrium phase which provides the proper average acceleration to maintain constant orbit radius. Associated with the phase oscillations are oscillations in energy and in orbit radius, which damp out rapidly as energy increases.

The ions are bunched by the phase oscillations into a sausage-shaped bundle which is centered on the equilibrium orbit and revolves at the resonant frequency around the orbit. The individual ions migrate around within this envelope following the phase oscillations. The applied frequency must match the theoretical value accurately to maintain constant equilibrium orbit radius. This requires a control system to program the applied frequency to a precision of about 0.1 per cent to keep the radial displacements within the useful aperture of the chamber.

The magnet is excited periodically, and ions are accelerated during the time that the magnetic field is increasing. The ions can be utilized when they reach maximum energy by distorting the frequency so that the orbit expands or contracts and particles strike a probe or an ejector device at the periphery. The magnetic field is then reduced to zero and the cycle repeated.

A preliminary test of the phase stability and focussing of the proton synchrotron was made at the University of California, using a one-fourth scale model of the Bevatron (7). All of the essential features were duplicated in the scale model except the peak magnetic field, so that it reached a final energy of only 6.5 M.e.v. However, most of the critical features of the design can be tested during the early part of the cycle. The model was successful in producing a high intensity beam, of the order of 10^8 protons per pulse under

the best conditions, an over-all efficiency of about 1/3 per cent. The stability of orbits was established for the "race track" design of four magnet quadrants with straight sections between quadrants. The effect on beam intensity of reducing the aperture was studied for three sizes. Qualitative information was obtained on the effect of varying the radio frequency rise time, and an optimum shape determined. The loss of intensity due to scattering by the residual air in the chamber was also measured. The results from this model study justify full hopes for the success of the full scale machines.

Design Features

The most complete published description of a proton synchrotron is for the Brookhaven "Cosmotron" (5). A few dimensions will be sufficient here to indicate the scope and size of the installation. Of more interest are some of the conclusions reached in the design study, and these will be discussed briefly.

The orbit radius for 3 B.e.v. protons in a magnetic field of 14 kilogauss is 30 ft. The magnet is constructed in four quadrants separated by 10-ft. gaps to allow straight sections of the vacuum chamber free from magnetic field to be used for injection, acceleration, and ejection of the ions. The over-all diameter of the magnet is about 75 ft. The magnet is assembled from 1/2-in. mild steel plate. In cross section, it looks like a block "C", with a 9 in. slot cut from 8×8 ft. octagonal plates to form the magnetic gap and to contain the exciting windings. The net aperture inside the vacuum chamber, which is located in the magnetic gap, is 30×7 in. This aperture was chosen after a theoretical study of the amplitude of betatron and synchrotron oscillations (9, 10), with practical allowance for errors and magnetic inhomogeneities. Choice of aperture determines magnet size and power requirements.

The magnet is powered from an alternating current generator and ignitron rectifier. The ignitrons are controlled to follow the magnet excitation cycle: one second to bring the magnet up to full field, and another second to reduce current to zero. Energy is stored in a large flywheel driven by an induction motor rated at 1,750 h.p.; the flywheel slows down during the 1 sec. magnet excitation and speeds up again when the stored energy of the magnet is returned to the flywheel during the following second. The total stored energy in the magnet is 1.2×10^7 joules at the peak of the cycle; about 10 per cent is dissipated in heat losses, largely in the water-cooled magnet windings. The motor makes up this loss and brings the flywheel up to speed between cycles. The cycle is repeated at 5 sec. intervals.

A horizontal electrostatic generator is used to produce pulses of 4 M.e.v. protons for injection into the Cosmotron orbit. The particles are deflected electrostatically into the outer periphery of the orbit at one of the straight sections. The initial free oscillations in the magnetic field and the orbit contraction due to increasing magnetic field are sufficient to allow a large fraction of the ions to miss the injector and settle into the equilibrium orbit. The

ion source is a high intensity "P.I.G." type pulsed for about 100 μsec.; pulse currents of 1 m.amp. of analyzed protons have been obtained in tests.

The electric accelerating field is provided by a radio frequency induction accelerator located at a straight section. A core of ferromagnetic ferrite material surrounds the vacuum chamber and is excited by a one-turn winding supplied by a radio frequency oscillator. This ferrite has the property of high permeability (mu about 1,000) at frequencies up to 4.2 megacycles. The frequency is programmed to match the desired range from 0.35 megacycles at the start to 4.2 megacycles at the end of the cycle, by an LC oscillator which has a saturable ferrite core inductance. This accelerating system is in principle a transformer with the proton beam acting as a one turn secondary.

The design of the magnetic field sets problems similar to those for the betatron and synchrotron. The field must decrease with increasing radius to provide focussing forces for the free oscillations of the ions. The range of the magnetic field index n for stability of both vertical and radial oscillations in circular machines is: $0 < n < 1$. For a wide horizontal and narrow vertical aperture and for a race-track orbit with straight sections, the range of n is: $0.5 < n < 0.8$. The design choice for the Cosmotron is: $n = 0.6$. Resonances between different modes of oscillation, which might feed energy into an undesired mode, are another limitation on n and have been carefully studied (10, 11).

Eddy currents in the iron due to the changing flux will distort the field, primarily at the start of the cycle; these effects are less severe for the 1-sec. cycle than for electron machines, and a lamination thickness of 1/2-in. has proven satisfactory. The remanent field must also be considered at injection; with the "C" magnet shape, it just counteracts the residual eddy current effect, a fortunate coincidence. The most serious problem is due to saturation of the iron at high fields which, because of the "C" shape, raises the value of n unduly. This is to be corrected by the use of pole face windings which will be pulsed by an auxiliary power supply as the magnetic field approaches its maximum value.

Twelve vacuum pump stations are located around the periphery of the chamber; tests indicate a possible operating pressure of 2×10^{-6} mm. Hg. This is low enough to make gas scattering losses negligible (12).

The building housing the Cosmotron has been designed to anticipate the problems of shielding personnel from the high energy radiations. The main floor on which the magnet rests is sunk below ground level, and control rooms and laboratories are on an upper level above the horizontal plane of the chamber where highest intensities are expected. Protection from scattered radiation can be added later if needed by erecting shielding blocks over the magnet.

The high energy protons can be ejected or directed against probe targets at the end of the 1-sec. acceleration interval. The anticipated intensity is of the order of 10^9 protons in each burst, at 5-sec. intervals. When using a probe or a magnetic "peeler," the protons will strike the target in a sequence of

several hundred pulses at the 4.2-megacycles frequency of ion rotation. Instruments for observing and analyzing the mesons from a target are under development.

Comparative Designs

Two of the machines under construction, the Cosmotron and the Bevatron, are of the "race track" design with four straight sections between magnet quadrants; the Birmingham and Canberra machines, on the other hand, have circular orbits. In the Cosmotron one of the straight sections is used for the ferrite induction accelerator; the Bevatron also utilizes a straight section for a "drift-tube" accelerating electrode. Circular machines must have the accelerating systems mounted in the magnetic field between poles, similar to the cavities used for the electron synchrotron, frequency modulated by external variable inductors or capacitors. A disadvantage of the straight sections is the increased length of path and the slightly larger aperture requirements. However, the advantage of increased flexibility of design and improved accessibility for testing and experimentation more than compensate for the disadvantages.

Four different low-energy accelerators are to be used as injection sources of protons. At Birmingham a Phillips Lamp Works voltage multiplier direct current accelerator for 2 M.e.v. is to be used for injection. At Brookhaven the source is a 4 M.e.v. electrostatic generator constructed by the High Voltage Engineering Company. At Berkeley a proton linear accelerator (Linac) for 10 M.e.v. is under construction. As previously mentioned, the Canberra machine is to have a synchrocyclotron of 200 M.e.v. as the first stage of acceleration. The advantage of high energy injection is considerable; amplitudes of radial and vertical oscillations decrease with increasing energy; therefore aperture dimensions can be reduced and with them the proportionate costs of magnet and power supply. In designing a machine, the aperture must be adequate to match the chosen injection energy.

Wide variations in magnet design have developed in the several laboratories. The Brookhaven "C" shaped magnet cross section, with the magnetic return circuit on the inside of the orbit and the outer face of the chamber exposed, greatly simplifies injection, ejection, and vacuum pumping problems and also provides the maximum access for experiments. This same feature is present in the Birmingham machine, with accessibility reduced somewhat by the necessity of introducing all leads and apertures through the outer face of the chamber. The Bevatron has a double magnetic return circuit similar in cross section to the standard cyclotron magnet. The advantage in this case is in reducing the problem of iron-saturation effects at high fields. The special feature of the Canberra cyclosynchrotron is the use of heavy current windings at the periphery of the synchrocyclotron magnet to produce very high fields (63,000 gauss) in an "air cored" magnet. The chief problem in this design is powering the air cored windings. This is to be accomplished at Canberra by utilizing the stored energy in the synchrocyclotron magnet, by incorporating a homopolar generator in the magnetic circuit.

In conclusion, it can be noted that the proton synchrotron raises the energy available from accelerators by a factor of 10 above present synchro-accelerators. Research in this energy range, formerly possible only with naturally occurring cosmic rays, is certain to result in new and important information about the phenomena of high energy reactions and the nature of nuclear forces.

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HIGH ENERGY ACCELERATORS

SYNCHROTRONS

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INTRODUCTION

The first published proposals for the resonance acceleration of charged particles to the extreme-relativistic range of energies appeared in 1944 and 1945. McMillan (58) at Berkeley and Veksler (76) of the U.S.S.R. independently realized that the principle of phase stability (as in the unwanted non-accelerating orbits of relativistic particles in the cyclotron) could be used to advantage to extend the range of available energies. A highly readable review of the fundamental principles of resonance acceleration at all energies has been given by Livingston (57), and no detailed exposition will be given here. Several theoretical discussions of the details of orbital stability in these machines are available (11, 29). Since the principles of orbital stability in the betatron apply in these cases as well, the betatron papers should also be considered fundamental to the discussion (47, 48).

The three main categories into which these accelerators fall are synchrocyclotron, electron synchrotron, and proton synchrotron. Each uses closed orbits in a magnetic guide field with radiofrequency (r.-f.) acceleration. The synchrocyclotron accelerates semirelativistic particles in a fixed magnetic field with large variation in orbit radius, accommodating the variation in period of rotation by frequency modulation of the accelerating voltage. The electron synchrotron on the other hand, accelerates only fully relativistic particles (for which $\beta \approx 1$) in an increasing magnetic field; thus, with constant-frequency accelerating voltage the orbit radius is constant and the guide field magnet can be kept small. The proton synchrotron accomplishes the acceleration of semirelativistic particles at constant orbit radius by increasing the frequency of the accelerating voltage simultaneously with the magnetic field.

In each of these machines the charged particles experience axial, radial, and phase focussing, or stated differently, they oscillate vertically and horizontally about some stable orbit position and the phase of crossing the accelerating gap oscillates about some mean value. For this to be true, the axial magnetic field B_z must decrease with radius but not more rapidly than $1/r$, i.e. $B_z = B_o(r_o/r)^n$ where $0 < n \leqq 1$. Also the peak available r.-f. voltage must exceed the energy gain per revolution needed by the particle to keep up with the increasing magnetic field.

The frequency of horizontal or radial oscillation is $\omega_r = \sqrt{1-n}\,\omega_o$ where ω_o is the frequency of rotation of the beam. The vertical frequency is $\omega_z = \sqrt{n}\,\omega_o$. The frequency of phase oscillation is small, being an order of

TABLE I

COMPARISON OF UNIVERSITY OF CALIFORNIA, CORNELL UNIVERSITY, AND MASSACHUSETTS INSTITUTE OF TECHNOLOGY SYNCHROTRONS (16, 35, 62)

	University of California	Cornell University	Massachusetts Institute of Technology
Magnet			
Type	Three leg	Distributed	Distributed
Weight of iron (tons)	135	75	50
Weight of copper (tons)	1.75	1.8	1
Lamination thickness (in.)	.014	.014	.014
Peak flux density (webers/$m.^2$)	1.14	1	1.2
Field index-n	0.67	0.67	0.7
Orbit radius, nominal (in.)	39.4	39.4	40
Gap height, pole to pole (in.)	3.7	3.25	2.9
Gap width $0<n<1$ (in.)	4.75	5.5	3.5
Coil, turns	32	20	18
Flux Bars			
Total cross section ($in.^2$)	214	209	210
Length (in.)	78	46	8
Lamination thickness (in.)	.002	.005	.014
Power Supply			
Type	Pulse	Alternator	Pulse
Repetition rate (pulses/sec.)	6	30	2*
Capacitor bank (μfd.)	818	1700	960
Resonant frequency (cycles/sec.)	32.1	30	45
Peak voltage (kv.)	19	11.2	15
Peak current (thousand amp.)	3.06	3.5	3.8
Energy input per pulse (kw.-sec.)	12.3	7	15
Vacuum Chamber			
Material	Fused quartz	Pyrex	Slip-cast steatite
Dimensions of opening (in. × in.)	2.63×5.38	$1\frac{7}{8}$×6	1.8×6.0
Joints	Rubber bands & stop cock grease	L shaped gaskets	Vinylseal
Internal coating	Air-drying silver #4817 (DuPont)	Laminated silver plate Aquadag between strips	Fired-on silver strips and india ink

* To be increased to 6 pulses per sec.

TABLE I—(*continued*)

	University of California	Cornell University	Massachusetts Institute of Technology
Radiofrequency Acceleration			
Oscillator type	Self-excited class C	Self-excited class C	Self-excited class C
Location of oscillator	Adjacent to magnet	Remote from magnet	Remote from magnet
Power tube type	Eimac 3X2500 A3	7C24	WL-530
Frequency (mc)	47.7	47.5	46.5
Peak power (kw.)	6	5.5	7.0
Gap voltage at loss of beam (kv., peak)	1.2	1.5	2.7
Operating gap voltage (kv.)	3.0	1.9	3.5
Electron Energies			
Injection (kv.)	100	80	80
End of betatron phase (M.e.v.)	2	2	7
Maximum at target (M.e.v.)	322	300	330
Central Beam Intensity (see p. 189)			
r per minute at 1 m. inside $\frac{1}{8}$-in. lead	1000	1600	180
r per pulse at 1 m. inside $\frac{1}{8}$-in. lead	2.8	0.9	1.5

magnitude less than the rotation frequency. The phase oscillation, essentially a variation in angular velocity, is accompanied by a radial oscillation of the same slow frequency.

As will be seen later, special precautions must be taken to insure that B_z and n do not have more than a certain minimum variation with azimuth angle θ. Also the radial component of field B_r must be zero in the median plane of the magnet to a high degree of approximation.

Because the problems of magnetic-field uniformity had been solved in the design of betatrons before McMillan and Veksler proposed the synchrotron, it was a straightforward matter to adapt an existing betatron for r.-f. acceleration; Goward & Barnes (36) in England made this adaptation and operated the first successful synchrotron at 8 M.e.v. Elder, *et al.* (27) at the General Electric Company had the first success in the high energy region with a 70-M.e.v. machine.

The section on SYNCHROTRON DESIGN AND OPERATION is a summary of of present practice in the design and operation of large electron synchrotrons emphasizing recent advances in understanding and with some proposals for the future. The section on the X-RAY BEAM discusses the x-ray beam, its

TABLE II

ELECTRON SYNCHROTRONS*

Location	Energy	Status
University of California, Berkeley, Calif., U.S.A.	322 M.e.v.	In operation
University of California Hospital, San Francisco, Calif., U.S.A.	70 M.e.v.	Under construction
California Institute of Technology, Pasadena, California, U.S.A.†	1000 M.e.v.	Under construction
Cornell University, Ithaca, N. Y., U.S.A.	300 M.e.v.	In operation
General Electric Co., Schenectady, N. Y., U.S.A.	80 M.e.v.	In operation
	300 M.e.v.	Under construction
Iowa State College, Ames, Iowa, U.S.A.	70 M.e.v.	In operation
Massachusetts Institute of Technology, Cambridge, Mass., U.S.A.	330 M.e.v.	In operation
University of Michigan, Ann Arbor, Michigan, U.S.A.	300 M.e.v.	Under construction (FM injection)
National Bureau of Standards, Washington, D. C., U.S.A.	180 M.e.v.	Under construction
Naval Research Laboratory, Washington, D. C., U.S.A.	No specific energy	Under construction
Purdue University, Lafayette, Ind., U.S.A.‡	300 M.e.v.	Under construction
Addenbrooke's Hospital, Cambridge, England	30 M.e.v.	In operation
Atomic Energy Research Establishment, Harwell, England (two)	25 M.e.v.	In operation
	25 M.e.v.	In operation
Glasgow University, Glasgow, Scotland	25 M.e.v.	In operation
	300 M.e.v.	Under construction
University of Johannesburg, Johannesburg, South Africa	13 M.e.v.	Under construction
University of Melbourne, Melbourne, Australia	20 M.e.v.	Under construction
Oxford University, Cambridge, England	140 M.e.v.	Under construction
Queens University, Kingston, Ontario, Canada	70 M.e.v.	In operation
Royal Cancer Hospital, London, England	30 M.e.v.	In operation
Royal Institute of Technology, Stockholm, Sweden	35 M.e.v.	In operation

* Betatron injection unless otherwise noted.

† The California Institute of Technology, with the support of the Atomic Energy Commission, is engaged in the construction of a large electron synchrotron using the magnet originally built for the quarter-scale model of the large proton synchrotron at Berkeley. New coils and a bevatron type power supply will be used to increase the magnetic field to about 5,000 gauss, using the large original vacuum tank which is about 3 ft. wide at a mean radius of curvature of 11½ ft. This will permit operation at about 0.5 B.e.v. Eventially the aperture and gap will be reduced by installing a new vacuum tank with pole tips in the vacuum, permitting operation at magnetic fields at or above 10,000 gauss and energies in the region of 1.0 B.e.v. It is planned

intensity, spectrum, angle of spread and pulse duration. A list of the known synchrotrons is given in Table II with status summaries for some of the larger machines. Table I gives a tabular comparison of the three largest synchrotrons in operation in 1950.

In the bibliography an attempt has been made to list all papers relating directly or indirectly to the subject which have been published since December 1, 1947. An excellent bibliography of material published prior to that date has been issued by the Brookhaven National Laboratory (12).

Synchrotron Design and Operation

Magnets—Most cyclotrons and betatrons and some synchrotrons use "three-legged" magnets with the gap in the center leg. Such a construction is reasonably economical if the entire region inside the orbit is to be filled with iron. However, in a synchrotron, the region inside the orbit is largely empty; thus, in order to avoid extremely long flux paths in the iron and to use the minimum amount of iron, it is wise to distribute the iron yoke around the orbit as uniformly as possible. All but one of the large synchrotrons so far constructed use distributed magnets.

In a distributed magnet the iron return path can be inside or outside the orbit, or partly inside and partly outside. In machines where flux from the guide field magnet is extracted for betatron acceleration (see p. 181), the flux return must be outside the orbit, since the net flux through the orbit must be in the same direction as the field at the orbit. (However, see p. 182.) Also in magnets of large aperture (ratio of linear dimension of space available for orbits to radius) there may not be room inside for all the return flux. Several magnets of small aperture for proton synchrotrons without betatron starting have been built recently with the flux return inside. One electron synchrotron magnet has been constructed with the flux return partly inside and partly outside the orbit (18). Another magnet with this structure was originally built as a model for the Berkeley proton synchrotron, and now is being adapted for an electron synchrotron (see footnote Table II).

Some magnets have been built in separated quadrants with straight sections in between to allow easy access to the region of the orbit as proposed originally by Crane (18). Special care must be used in the design of these separated magnets to insure that the particle orbits will be stable. For example, the azimuthal variation in B can cause resonance between the radial and vertical oscillations for several critical values of the magnetic-field index, n (23, 24, 25). Also, when $n \approx \frac{3}{4}$ or $\frac{1}{4}$ the azimuthal variation in n can cause a resonance in which the radial oscillation absorbs energy from the orbital

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to inject electrons at 1.5 mv from an external electron gun driven by a high voltage pulse transformer.

‡ The Purdue 300 M.e.v. electron synchrotron is undergoing initial tests and adjustments. At this writing betatro operation has been achieved. In many respects this machine is similar to the Massachusetts Institute of Technology accelerator.

motion unless the first harmonic of $n(\theta)/n_o < 10^{-3}$ (17). These requirements of course, apply to magnets of any design, but they may be especially difficult to meet in a magnet which has unavoidable azimuthal irregularities.

Since the vertical focussing oscillations of the electron beam are caused by small oppositely directed radial components of the magnetic field above and below the stable orbit, any over-all B_r will neutralize part of the vertical focussing field and raise or depress the equilibrium orbit. Thus, special precautions must be taken to keep B_r small.

Except in magnets of extremely careful design, remanence and eddy currents will cause the magnetic field in different portions of the gap to differ in time phase by small amounts. Thus, at any point, the magnetic field can be separated into a component in phase with the exciting current and a component 90° out of phase. When the average field is near zero as at injection time, the out-of-phase components can easily be dominant and the values of n, B_r, $n(\theta)$ and $B(\theta)$ may be entirely unsuitable. These difficulties can be corrected by appropriately placed windings which carry small currents out of time phase with the current in the magnet windings. In the Massachusetts Institute of Technology machine, for example, windings above and below the vacuum chamber in the magnet gap have been provided to vary n and B_r, and windings around portions of the magnet yoke are used to vary $B(\theta)$. The design of the latter follows that first used at Cornell, allowing the first and second Fourier components of $B(\theta)$ to be varied with only four controls, one each for corrections proportional to $\sin\theta$, $\cos\theta$, $\sin 2\theta$, $\cos 2\theta$. Although the main magnet windings are pulsed, it has proved satisfactory to excite the out-of-phase windings from the 60-cycle lines with Variac control. The initial determination of values of these correction currents was tedious, but no major changes have been required, even when the magnet is taken down and reassembled.

Kerst has succeeded in the construction of a magnet for his 300-M.e.v. betatron which has remarkable properties (50, 51). He has made each lamination which carries guide flux to the orbit the same length, and he has allowed practically no gaps between laminations at the orbit. By this procedure, eddy-current and remanence effects have been equalized for all portions of the gap and azimuthal inhomogeneities have been eliminated so that no correction windings whatever are needed. In fact, the indication is that auxiliary windings would only be harmful. Certainly, anyone planning a new machine should give careful consideration to the principles he sets forth.

Although the magnet of these machines usually uses an iron yoke, pulsed magnets without iron have been proposed (44), and one is undergoing preliminary tests at the General Electric Company (33). The ironless magnet, having no saturation limit, can be made smaller for a given peak output energy and probably requires no more stored energy. It has little or no eddy currents and no remanence to distort the shape of the weak magnetic fields near injection time. However, it requires extremely large currents and its energy dissipation is large unless the accelerating cycle is short. Its chief dis-

advantage is the mechanical force on the conductors; this probably sets an economic upper limit of 500 M.e.v. Probably the ironless machine is most economical in the 100 M.e.v. region. For example, Kaiser & Tuck (44) believe that an 85-M.e.v. accelerator could be built with 12-cm. radius and 10^4 joules stored energy.

Preacceleration to $\beta \approx 1$.—Some means must be found in the electron synchrotron to inject the electrons into the constant-frequency synchrotron phase at approximately the velocity of light. The method most commonly chosen is betatron acceleration in the field of the synchrotron magnet (16, 27, 34, 36, 62, 65). The betatron flux customarily is supplied by flux bars attached to the poles of the guide field magnet. These flux bars are in operation for only the first few hundred microseconds of the acceleration cycle, after which they become saturated and have no further effect.

Since the rate of rise of flux density in the flux bars is greater than in the iron of the magnet, the flux-bar eddy currents are also greater. In a pulsed machine these eddy currents have a rise time of several microseconds during which they reduce the apparent permeability of the iron. In the main magnet, the flux density depends primarily on the air gap and not strongly on the apparent permeability, but in the flux bars the air gap is small and a variation in permeability there will adversely affect the betatron flux condition (50). Thus, the rate of rise of flux density and the small flux-bar air gap can work together to delay the establishment of conditions for stable electron orbits beyond the normal time for injection. This difficulty is avoided by reverse biasing the main magnetic field. The time for the field to build up to zero can be made long enough so that eddy-current transients are gone by injection time. Direct current through the main magnet windings or in special windings provided for the purpose can be used for the reverse bias. A series inductor must be used to keep induced voltage out of the D.C. source.

The position of the stable orbit depends on the amount of flux carried by the flux bars as a function of time (i.e., on the betatron condition). A coil around the flux bars connected to a variable inductor gives good control over the flux condition, since the linearly rising current through the coil and inductor cancels some of the ampere turns of the main winding.

The 300-M.e.v. betatron at the University of Illinois (50, 51) uses an entirely separate magnetic circuit to supply the flux for acceleration. This is a three-legged core which completely encircles the guide-field magnet. A proper distribution of the D.C. bias windings and an extended copper shield under the A.C. windings, insure that no flux leaks from this core to affect the guide magnet. The conspicuous success of this betatron raises the possibility of the use of a D.C. biased flux loop entirely separate from the guide field magnet to supply the betatron flux for the initial acceleration in a synchrotron. Of the many ways in which the exciting current for this flux loop could be obtained, one of the most attractive would be a "flux-forced" winding whose voltage would be maintained at a fixed fraction of the main magnet voltage, possibly by a feed-back circuit. Of course, this winding could not be

connected in parallel with the main magnet, since in a synchrotron the flux loop would be expected to saturate early in the acceleration cycle; however, since the amount of stored energy required for initial acceleration is very small, this flux-forced winding could be supplied with current from high-emission vacuum tubes. A rough calculation indicates that 50 amp. peak at about 20 kv. with a duty factor of 10^{-4} should be adequate to supply flux for a 300-M.e.v. synchrotron at six pulses per second when the rate of rise of the main magnetic field corresponds to 60-cycle operation.

Further, if a separate core were used for the betatron flux, the synchrotron designer would be freed from the necessity of having the magnet return yoke outside the orbit if he wished to use betatron starting. Of course, it would only be possible to have the magnet return path inside the orbit in a machine of relatively small aperture, such as that now under construction at the California Institute of Technology. The reverse flux in the guide magnet return would increase the necessary size of the betatron-flux core only a little, since even in a machine of large aperture the flux change in the guide field magnet is only one-third of the flux change in the core during the betatron phase (50).

Wilkins (79) has given a detailed discussion of the magnetic aspects of flux-bar design. Other problems to be considered in planning flux bars are these: their effect on the guide field, obstruction of access to the vacuum tube, and difficulties of mounting.

To avoid some of the betatron problems, Crane proposes to inject the electrons from an external accelerator at $\beta \approx .87$ (500 kv.) and to use frequency modulation to keep the orbit radius constant (18, 19). Langmuir (see footnote Table II) plans to inject from an external source at $\beta \approx .97$.

Kaiser & Tuck (44) have suggested a novel method for covering the region $\beta < 1$. If ω is the fixed frequency of the accelerating voltage, they propose to let $\omega = m\omega_o$ where m is an integer and ω_o is the frequency of rotation of the electrons. In a particular machine, m might have a maximum value of 5. Electrons would be injected at $\beta = 0.4 = \frac{2}{5}$ (45 kv.) corresponding to $m = 2$. The radiofrequency would be turned on and as β increased the orbit radius would increase proportionally. When β became so large that further increase in radius would cause loss of the beam, the radiofrequency would be turned off and the orbit radius allowed to decrease as the magnetic field continued to increase. The radiofrequency would be turned back on at $m = 3$ when the radius had shrunk to the appropriate value. Two more off-on cycles would bring m to its final value after which the radiofrequency would be left on for conventional synchrotron acceleration (see p. 185).

Magnet excitation.—The alternating current for the magnet can be obtained from the power lines (27), from an alternator (16), or from discharge of a capacitor bank (34, 62). Continuous A.C. excitation requires a great deal of power and provision must be made to remove the heat generated in the magnet (16). If the duty factor is small, pulsed excitation requires less average power and allows smaller conductors to be used in the magnet wind-

ings with a considerable saving both in copper and in iron. Pulsed excitation requires more complex control equipment (35, 62) and of course gives less average x-ray output.

Capacitors are used to store energy for these magnets. In the case of continuous A.C. excitation, the capacitor and magnet resonate at the frequency of the exciting voltage; so the line current merely supplies the losses in the system. Since the inductance of the magnet is a function of its peak excitation, some method of tuning must be used to insure that excessive line currents will not be drawn when the power is turned on.

In pulsed operation, the capacitor is charged from a D.C. source and then discharged into the magnet. If one cycle of oscillation is allowed per pulse, the capacitor will return each time nearly to its initial voltage. Between pulses the D.C. source supplies the system losses. Apparently a given capacitor can be used in low-duty-factor pulse service at much higher rating than in continuous duty, an economic factor in favor of pulse operation (35).

The University of Illinois 300-M.e.v. betatron operates (50, 51) for only one-half cycle per pulse. The average power drain is only half of the full-cycle-operation drain, but each pulse reverses the capacitor voltage. Between pulses before the capacitor can be recharged from the D.C. source, the capacitor polarity must be reversed with a mechanical switch. Since the D.C. source must be off while the reversing switch operates, grid-controlled rectifiers are used. This procedure should be equally useful in synchrotron systems.

In pulse service it is customary to use ignitrons to control the capacitor discharge, since no other suitable means is available. In the Massachusetts Institute of Technology machine, GL-506 ignitrons are used. These withstand 20 kv. peak inverse and each tube carries 2,000 amp. peak.

It has been reported (33, 55a) that the GL-506 will carry much larger peak currents without damage, but certain precautions must be taken. If the ignitron is operated at high current in the presence of the magnetic field from nearby conductors and for long pulse periods (e.g., "30-cycle" pulses or half sine-waves lasting 1/60 sec.), there is a tendency for the arc to transfer from the mercury pool to the wall of the tube, with eventual destructive effects. Measurement of the voltage drop in the tube wall can be used as a danger signal for these effects. They apparently can be avoided by providing a magnetic shield around the ignitron and by properly situating the heavy-current-carrying bus bars.

Various transients arising in the magnet and ignitron system because of stray capacitance and inductance must be controlled with suitable damping networks. One serious transient occurs when the ignitrons first begin to conduct, suddenly applying voltage to the magnet terminals. This transient may be readily visualized as the resonance of the stray capacity of the magnet with the inductance of the leads from the ignitrons and capacitor bank. It is easily damped out by connecting a capacitor and resistor in series across the magnet terminals. The capacitor should be three or four times the mag-

net strays and the resistor correct for critical damping with the lead inductance.

Another transient of importance arises at the end of conduction when the inverse voltage builds up across the ignitrons. In this transient the full inductance of the magnet resonates with the stray capacitance of the leads. Again the problem can be solved by an appropriate series combination of resistance and capacitance, in this case across the ignitrons. This capacitance should be three or four times the lead capacitance. The resistor may be chosen for critical damping, but if the transient is not completely damped it can be of use in reducing remanent flux in the magnet.

Vacuum and vacuum chambers.—The vacuum chambers of the electron synchrotrons now in operation are donuts of ceramic, glass, or quartz. In the large machines (22, 74), these are made up of segments joined together in various ways. These tubes must always be coated internally with conducting material to carry away stray charges. Goward, *et al.*, have given an estimate of the minimum usable resistivity for such a coating (39). Nonconducting patches on the tube wall cause loss of the beam in many cases. Their effect is not always predictable, hence they are avoided in so far as possible.

In the large operating synchrotrons, a vacuum of 10^{-5} mm. of mercury or better is usually maintained. The beam intensity decreases with increasing pressure and is nearly zero at 10^{-4} mm. Hg.

Watson (77) has made quantitative measurements on the betatron phase of a 30-M.e.v. synchrotron. He finds that the intensity, I, obeys the empirical equation

$$I = I_o \exp(-1.1ptv^{-1/2})$$

where p is the air pressure in millimicrons of mercury, t is the accelerating time in milliseconds, and v is the injection voltage in kilovolts. This formula predicts that the beam will survive at somewhat higher pressures than are found in practice with the large machines. Probably the tolerable multiple scattering angle for electrons in the small machines is greater than in the large because the vacuum tube aperture usually is smaller in the large machines.

Radiofrequency acceleration.—The r.-f. acceleration is accomplished in presently operating machines by passing the beam through a resonant system resembling that of a klystron. The most convenient form consists of one section of the donut, coated internally, externally, and across one end with highly conducting material and resonated in the coaxial mode (16, 22, 27, 74). To avoid the induction of large eddy currents in the conducting layer by the magnetic guide field, the coating is separated into strips. Cuts approximately parallel to the direction of r.-f. current flow can be made to have a negligible effect on resonator Q if they are carefully laid out.

In these resonators high r.-f. voltages exist between the sharp edges of the coating across short insulating gaps. At the Massachusetts Institute of Technology it has been useful to terminate the coating in small rounded

electrodes which completely cover the sharp edges. The presence of these electrodes raises the breakdown voltage of the gap a factor three in some cases.

Kaiser (45) has recently analyzed the conditions prevailing at the time of transition from the betatron phase of acceleration to the synchrotron phase; i.e., when the r.-f. voltage is turned on. From his analysis it appears that in synchrotrons of small aperture and with high Q resonant r.-f. systems, 100 per cent of the electrons in the betatron orbit should be trapped into the synchrotron phase. In a high Q system the r.-f. voltage build-up time will be of the order of Q cycles. Given a build-up time this long, Kaiser shows that the initial phase at which an electron crosses the r.-f. gap is not important, but that the critical parameter is the phase-velocity; i.e., the difference between the angular frequency of the particle and the angular frequency of the oscillator. Since the angular frequency of the particle at this time depends primarily on its radius, in a machine of small aperture the phase-velocities can be kept small.

Kaiser & Tuck (46) have tested this theory of electron capture by turning off the r.-f. accelerating voltage of a 14-M.e.v. synchrotron for a period long enough to allow the electrons to become uniformly distributed in phase. When the accelerating voltage was re-established all electrons were recaptured except those whose phase velocities were too great, exactly as predicted.

The average radius depends on the amount of flux in the flux bars and because of the variable permeability of the flux-bar iron, the radius will usually be changing at the time the r.-f. voltage is turned on. Thus, assuming sufficient r.-f. voltage, three things can affect the efficiency of capture: first, the frequency of the accelerating voltage; second, the average flux in the flux bars; and third, the time at which the r.-f. voltage is turned on.

Electron guns for injection.—Stone (72) has adapted a new cathode material developed by the Raytheon Manufacturing Company to the purposes of injection into the betatron phase. The Raytheon cathodes consist of a molybdenum-thoria mixture sintered in the form of cylinders of $\frac{3}{8}$-in. diameter. These have sufficiently high resistance to be directly heated. A $\frac{3}{8}$-in. by 1/16-in. sliver cut longitudinally from one of these cylinders is substituted for the usual tungsten spiral of the conventional injector. The concave side of the sliver is used as the emitting surface. With the proper geometrical arrangement, these injectors will give a beam in which half the total emission deviates less than 2° from the axis and they will easily emit up to 1 amp.

Electron guns of this type have been in use at the Massachusetts Institute of Technology for the past year. Since the output of the synchrotron falls off when the emission from the gun is increased beyond 200 ma., further improvements in gun focussing appear to be unnecessary.

Stone also found that an intermediate electrode between cathode and anode in the injection guns increased the breakdown voltage by 60 per cent. The additional electrode was maintained at a potential midway between the

cathode and anode potentials. Presumably, the improvement in breakdown voltage is attributable partly to "the total-voltage effect" in vacuum insulation and partly to the reduction of the electric field at the cathode, which inevitably has some points of extremely small radius of curvature.

Advances in understanding of injection into betatron.—For some time, the mechanism of injection into betatrons (and synchrotrons) has been something of a mystery, since a calculation from simple theory shows that the electrons should all strike the injector structure after about 10 revolutions. Recently, however, Kerst (49, 50) has given an explanation of the factors which are normally involved in injection, and ways in which special field disturbances can be of aid have been described by Jones, *et al.*, (43) by Davis (21), and by Davis & Langmuir (20). Fundamentally all these processes are of two kinds: in one, the equilibrium orbit is displaced away from the injector in a time corresponding to about 10 revolutions; in the other, the amplitude of the radial oscillations is reduced in a similar period.

The mechanisms given by Kerst involve both processes. First, he points out that the electron-beam current flows in a direction to reduce the flux in the flux bars. Of course, the sudden establishment of the beam current must be accompanied by current changes elsewhere in the system, but the net effect is to momentarily destroy the betatron condition and to cause the beam to spiral in and away from the injector more rapidly than would a single electron in the absence of the rest of the beam. It has been found, in confirmation of this mechanism, that a pulse of current in the same direction as the beam current but in a wire wound about the flux bars is useful in increasing the number of trapped electrons. Such windings are called contractor coils.

Kerst's second mechanism involves the space-charge self repulsion of the beam. Most of the initially injected electrons are eventually intercepted by the injector, but it is just this loss of space charge which makes possible the survival of the remainder. The space charge, giving forces opposite in direction to the normal guide field magnetic forces which tend to return the electrons to their equilibrium orbit, causes the radial (and vertical) oscillation frequencies to be less than normal. As the space charge is gradually removed these frequencies increase and the amplitude of oscillation correspondingly decreases. This variation in space charge is equivalent to a variation in the effective value of n.

Since both of the mechanisms suggested by Kerst depend on the presence of charge circulating in the orbit, it might be expected that the output of a betatron would increase as $(I)^p$, where I is the injected electron current and p is greater than one. That this is true was shown by Westendorp & Elder (78) for three betatrons.

Davis (21) proposes that $B(\theta)$ be given a transient variation to distort the equilibrium orbit away from the injector structure in a period of the order of ten revolutions. At Berkeley (63a) it was found that a pulse of current at injection time in a coil around $\frac{1}{8}$ of the pole face considerably in-

creased the output. The operation of this octant coil is probably explained by the mechanism suggested by Davis.

Jones, *et al.* (43), and Davis & Langmuir (20) have suggested that n be made to vary with azimuth by appropriately placed windings, and that the average n be adjusted to $\frac{3}{4}$ so that the radial oscillation frequency $\omega_r = \frac{1}{2}\omega_o$. By this means it is possible to increase the restoring force on the electrons whenever they are traveling away from the equilibrium orbit and to decrease the force while they travel toward equilibrium. The amplitude of radial oscillation will thus decrease. Again $n(\theta)$ must be a transient variation since if it is maintained, the phase of the radial oscillation will slip and the oscillation amplitude will build up again. The same principle can be applied to the vertical oscillations, provided that the average n be $\frac{1}{4}$ so that $\omega_z = \frac{1}{2}\omega_o$. The group at General Electric have found this method quite useful in practice.

It may be that the method of variation of $n(\theta)$ may be incompatible with the space-charge mechanism since in the latter the average effective value of n is not constant in time.

The simplest of all injection mechanisms comes into play only for those large accelerators where the voltage gained per revolution by the electrons is a significant fraction of the injection voltage. In fact, if the electrons are injected so that their instantaneous stable orbit deviates from the betatron orbit by an amount Δr, then the instantaneous orbit will approach the betatron orbit by an amount δ per turn where $\delta/\Delta r = \Delta E/E$, ΔE being the energy gain per turn and E being the injection energy. It is probably significant that the accelerator which gave the least difficulty in its initial tests was the first one for which δ could be as large as 2 mm. (50, 51).

In the design of a large accelerator then, since E must be kept large to avoid difficulties from eddy-current and remanence fields, ΔE should be maximized to help in missing the injector. In the usual design of betatron-started synchrotrons, the presence of the flux bars in the magnetic circuit slows down the initial rate of rise of magnetic field so that ΔE is smaller initially than it is later when the flux bars are saturated. If a separate flux core were used (see p. 182) with its own flux-forced excitation, the initial rate of rise of magnetic field could be increased by at least a factor 3.

Finding the beam.—There has been a great deal of informal discussion between groups on the problem of first finding the beam in a synchrotron. In what follows, the Massachusetts Institute of Technology experiences will be recounted, but without claim of originality.

The initial tests of a synchrotron are facilitated by the use of a scintillation crystal inside the vacuum system. The light from this crystal is carried by a lucite light pipe to a photomultiplier well outside the magnetic field. The crystal and the portion of the light pipe inside the vacuum system have a conducting coating; 2-mil aluminum foil over the crystal and DuPont #4817 conducting silver on the lucite have proved satisfactory. Various scintillators have been used, but the common materials are subject to such serious afterglow that a feeble beam which lasts 10 or 20 μsec. may not be

detected because of the glow left over from the "main bang" of injection. Some work was done by Lewis (56) at the Massachusetts Institute of Technology to find a phosphor with better than average afterglow characteristics. The inorganic phosphors, including fuzed quartz, were all uniformly poor in this respect. Of the organic phosphors, diphenyl-acetylene[1] and chrysene seem promising although they have not been tried in the synchrotron. Also the terphenyl-polystyrene solution developed by Schorr (68) may be useful. It should be noted that for this use the afterglow characteristic is much more important than the total light output. In the choice of a scintillator, vapor pressure must also be taken into account.

The three large synchrotrons now in operation were all initially operated successfully at low magnet excitation, about 1/10 maximum or less. This seem to be the most satisfactory way to reduce the effects of remanence and eddy currents. Once the presence of a betatron beam is detected (by its collapse against the internal scintillator), it is usually easy to increase the magnet excitation gradually without irreparable loss of the beam.

In any case, the first task is to get electrons around the magnet once. Injection timing and to some extent magnetic-field shape are important here. Build-up of stray charges on the donut walls may manifest itself by fluctuations in the main-bang signal on the scintillator, if the latter is placed to measure the beam which has gone once around.

It is possible to separate the effects of electrons which go around the magnet once from those of electrons which make more than one circuit, even though phosphor afterglow conceals the structure of the scintillator pulses. A horizontal electric deflecting plate (potential about 2,000 v.), downstream from the scintillator and upstream from the gun, can be used to block the beam after it passes the scintillator. When the plate is grounded, most of the beam will get by it, for a possible few revolutions at least. Thus, the increase in scintillator signal when the plate is grounded is a measure of the beam which travels more than once around the orbit before being lost.

On the Massachusetts Institute of Technology machine it has been possible to detect the presence of electrons which make 30 or 40 revolutions by a periodicity in the scintillator signal corresponding to twice the rotation period, or about 0.1 μsec. Apparently the beam is bunched to some extent and the radial oscillations (for $n \approx \frac{3}{4}$) have a minimum at the scintillator every second revolution. This periodicity is much easier to detect in the presence of afterglow than gradual nonperiodic collapse of the beam.

When the beam has survived for 20 or 30 μsec., it is useful to force it all to hit the scintillator quickly by discharging a condenser into a winding around the flux bars to give reverse betatron flux. Again, in the presence of afterglow this sharp pulse is more easily detected than an extended pulse resulting from gradual collapse.

[1] Ravilous, Elliot & Liebson have shown that diphenyl-acetylene is an excellent phosphor (65a).

At the Massachusetts Institute of Technology when full betatron action was obtained, synchrotron action appeared without further difficulty. Also, it has never been necessary to return to low excitation since full scale operation was achieved, even though the magnet has been taken apart and reassembled twice in the interim.

Initial operation of the Massachusetts Institute of Technology machine was not facilitated by special transients at injection time. Success first came after the interior of the donut was coated with India ink to help conduct stray charges from the insulating gaps in the metallic coating. Later evidence indicates that not all insulating patches are harmful, especially if they are some distance from the injector.

The X-Ray Beam: Measurement, Characteristics, and Control

Measurement of beam intensity.—There are three more or less absolute methods for measuring the energy in a beam of high-energy x-rays. The first and most direct method, used at the University of Illinois (52), is to absorb the entire beam in a calorimeter.

The second method, developed at Berkeley by Blocker, Kenney & Panofsky (10), consists in measuring the energy lost by ionization when the beam is completely absorbed. This is accomplished by varying the position of a thin ion chamber in an effectively infinite absorber. The ionization is a measure of the number of shower electrons at any given depth in the absorber. Since the mean energy loss of an electron per unit path in the absorber is known, numerical integration gives the total energy in the beam. If the ion chamber is thin enough and broad enough so that no electrons escape from its edges, the effect of electrons traveling at angles to the normal is automatically taken into account. If not, ion chambers of various thicknesses must be used and the measurements extrapolated to zero thickness.[2]

The third method, also developed by the Berkeley group (10), gives a measure of the pair-production by the x-ray beam. We assume that the ionization behind a converter is due to three portions, the background, the Compton electrons, and the pair electrons, and that the background and Compton ionization is a function only of N_e, the number of converter electrons per square centimeter, while the pair ionization can be expressed as proportional to N_e times a function of Z, the atomic number of the converter. If so, then it is possible, by measuring the ionization behind converters of the same N_e but different Z, to separate the pair ionization from the rest. The converters must be so thin that absorption of the x-ray beam and radiation

[2] Another result of the above research well worth noting is that beyond a certain depth of converter (or absorber), the ionization density falls off exponentially in accordance with the minimum absorption coefficient for γ-rays. In lead, for example, the maximum ionization comes at about 18 gm./cm.^{2}, and beyond about 30 gm./cm.^{2} the ionization decreases a factor 2 in each 20 gm./cm.^{2}.

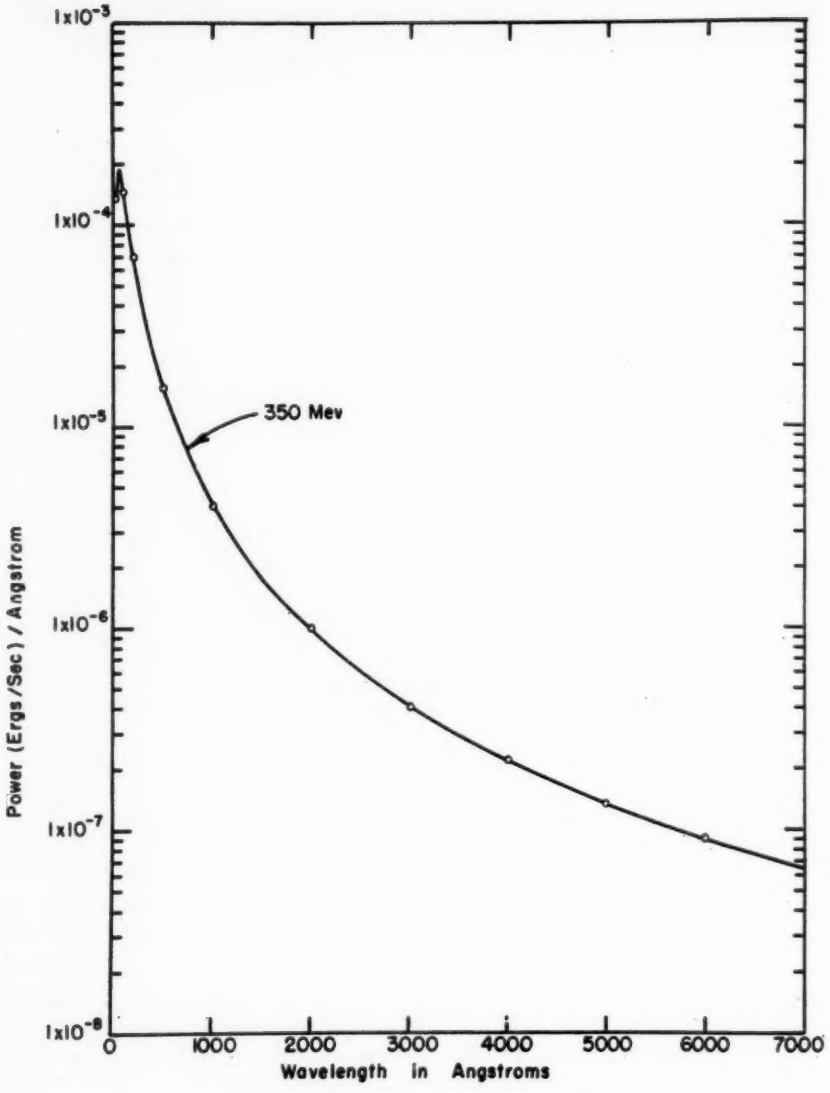

FIG. 1. Light spectrum over one cycle.

from the electrons are negligible. Less than 5 per cent error from these sources will result if $N_e/N_o < 0.1$, where N_o is Avogadro's number. Also, the most accurate results will be obtained for converters of large difference in Z. Detailed corrections to the method for the case of large N_e and for various pairs of converter materials are given in the original paper.

Within the above limitations, the beam strength can be calculated as follows: Let Q be the number of effective quanta. ($Q = U/k$ where U is the total beam energy and k is the maximum photon energy.) Let I_1 be the ionization per unit area behind converter 1 and I_2 that behind converter 2. If I_o is the ionization per electron per unit path in the gas of the ion chamber, g is the ion chamber thickness and ϕ_p is $1/Z$ times the cross section for pair production per atom, per effective photon averaged over the photon spectrum, then

$$I_1 = QI_og[2N_e\phi_{p_1} + f(N_e)]$$

and

$$I_2 = QI_og[2N_e\phi_{p_2} + f(N_e)]$$

where $f(N_e)$ is a measure of the ionization due to Compton effect and background and depends only on N_e. Therefore,

$$Q = \frac{I_2 - I_1}{2I_ogN_e(\phi_{p_2} - \phi_{p_1})}$$

ϕ_p has been given by Blocker *et al.* (10) and is tabulated in Table III.

TABLE III

AVERAGE PAIR PRODUCTION CROSS SECTION PER ELECTRON FOR *Bremsstrahlung* FROM 330-M.E.V. ELECTRONS (10)

Z	6	13	29	82
$\phi_p/(Z+1)$	2.54×10^{-26}	2.55×10^{-26}	2.50×10^{-26}	2.20×10^{-26}

Although ϕ_p has been evaluated for a particular spectrum (330-M.e.v *Bremsstrahlung* from 0.020 in. of platinum) its value is not sensitive to the detailed shape of the spectrum (63a). Of the three absolute methods outlined above, only the last is independent of electron contamination in the beam.

Various other means have been used to express the intensity of the x-rays from the synchrotron in terms of the r unit, familiar in radiation therapy. The r unit is defined in terms of a beam of photons in equilibrium with its secondary electrons. For 300-M.e.v. x-rays no equilibrium can be established, and the "air-wall" ion-chamber practice applicable at lower energies is not useful. In fact, any measurement of high-energy x-rays with an r meter depends strongly on the amount of electron contamination in the beam, the shape and location of converters and the presence of back scatterers. McMillan, Blocker & Kenney (61) have proposed a standardized r measurement and have made cross calibrations with the absolute methods. They have used a Victoreen thimble meter inside a lead cylinder 2 in. long, $\frac{5}{8}$-in. inside diameter, and $\frac{1}{8}$-in. wall thickness. The thimble and cylinder are

placed transverse to the beam and far enough from the synchrotron so that the beam is effectively uniform over a region at least an inch wide. Table IV gives these calibrations for the Berkeley machine, where the thimble readings are given in r.

Angle of spread and spectrum.—The output of the synchrotron is a narrow beam of x-rays whose spread decreases with increasing electron energy. Stearns (71) has calculated the root-mean-square angle of spread for *Bremsstrahlung* in the thin-target case. His result is $\theta_{\text{rms}} = k(mc^2/E)\ln(E/mc^2)$ where m is the rest mass of the electron, E is the electron energy, and $k = .65 \pm .15$ over wide ranges of electron energy, photon energy and target material. The detailed variation of k is given in Stearns' paper. The expression given above for θ_{rms} was calculated using $\theta_{\max} = 20°$ for the limit of integration. Stearns

TABLE IV

VICTOREEN THIMBLE CALIBRATIONS FOR BERKELEY SYNCHROTRON (61)*

x-ray energy	ergs/cm.$^2 \cdot r$	M.e.v./cm.$^2 \cdot r$	"effective quanta"/cm.$^2 \cdot r$
320 M.e.v.	5.3×10^3	3.3×10^9	1.04×10^7
160 M.e.v.	3.5×10^3	2.2×10^9	1.38×10^7

* Thimble inside $\frac{1}{8}$ in. of lead.

gives the correction to θ_{rms} to be applied when $\theta_{\max}$ is chosen different from 20°.

When a 0.060-in. tungsten wire is used as the target, the intensity of the x-ray beam from the Massachusetts Institute of Technology synchrotron is half the axial maximum 0.3° from the axis. The actual value of θ_{rms} is certainly several times greater than 0.3° but is difficult to measure because it depends strongly on the feeble intensities at large angles. θ_{rms} from Stearns' formula should be about 0.3°; presumably, the scattering of the electrons in the target material accounts for the added spread of the x-ray beam. The electron beam approaches the target so slowly that it can strike no farther from the target edge than a few thousandths of a centimeter; thus, only a carefully aligned target of rectangular cross section could be said to have a well defined effective thickness. The Berkeley group have used a platinum foil 0.020 in. thick as the target. They state (63a) that the angular beam spread can be explained adequately on the assumption that the electron beam penetrates the full target thickness.

Also at Berkeley, Hartsough, Powell & Hill (41) have shown by cloud chamber methods that the x-ray spectrum agrees with the theoretical *Bremsstrahlung* energy distribution for their 0.020-in. platinum target. The theoretical distribution is given by Blocker *et al.* (10). This result and the abso-

lute-intensity measurements have made quantitative nuclear-cross-section experiments possible.

X-ray pulse duration.—The most simple way to cause the electrons to strike the target is to turn off the r.-f. voltage. The beam then spirals in to smaller radii as the magnetic field increases, or if the magnetic field is constant (i.e., at maximum) the electrons spiral in as they lose energy by central-acceleration radiation. Under these conditions, the x-ray pulse lasts about 10 μsec.

For some purposes (see p. 194) it is desirable that the x-ray pulse be as short as possible. If, just before the beam strikes the target after the r.-f. voltage is turned off, the magnetic field is increased on one side of the machine and decreased on the other (15), beam oscillations are set up which force all the electrons into the target in as little as 1 μsec.

On the other hand, it is frequently desirable to spread the beam out over as long a time as possible (see p. 194). One way is to turn the radio frequency off after the magnetic field has passed its maximum. A time can be found such that the tendency of the beam radius to decrease because of central-acceleration radiation is almost balanced by the effect of decreasing magnetic field. The beam then spirals in so slowly that the x-ray pulse lasts about 100 μsec. Because the magnetic field must be past maximum, the electrons have lost about 10 per cent of their maximum energy by the time they hit the target.

A better method for lengthening the pulse is to decrease the r.-f. voltage gradually. The electrons having the greatest amplitude of phase oscillation are lost from the beam first. Since there is always a distribution of phase-oscillation amplitudes, it is possible to stretch the pulse out over a long period. Pulses as long as 2,500 μsec. have been obtained by this method (22).

Optical radiation.—Since the electrons in the synchrotron continuously undergo central acceleration, they must radiate (28, 59). This steady radiation extends throughout the optical spectrum with considerable intensity in the visible and a great deal more in the far ultraviolet. Figure 1 shows the energy distribution per wavelength interval of the radiation averaged over the acceleration cycle of the synchrotron as calculated from the theory given by Schwinger (69). It is to be noted that the maximum energy per wavelength comes in the neighborhood of 70 Å. Thus, it is expected that this radiation will for the first time make possible the accurate measurement of absorption spectra and absolute line-spectrum intensities in the region 50 to 200 Å.

The total energy lost as central-acceleration radiation increases with the fourth power of the electron's energy. In the visible region, however, for an orbit radius of 1 m., this radiation becomes noticeable at about 60 M.e.v. and levels off at about 200 M.e.v. To the eye, this radiation appears brilliantly intense. At the Massachusetts Institute of Technology the light has been photographed using a rotating drum camera with an f-11 lens 2 m. from the orbit. Complete blackening of the film was obtained with 5-μsec. exposures.

The intensity and duration of this light make it useful as an indicator of the strength of the synchrotron beam. A photoelectric detector may be used several meters from the machine without lenses and without excluding the general laboratory illumination.

Use of the Synchrotron

It is the purpose here to discuss briefly those special problems which arise in performing counter experiments using synchrotron-produced radiation. Actually, of course, similar problems are associated with the use of other pulsed devices such as betatrons, synchrocyclotrons, etc.

All but a very few special or simple counter experiments involve measuring time coincidences between events in one or more counters. As discussed in a previous section, the duty cycle of typical synchrotrons is small. Other things being equal, a small duty cycle clearly increases the relative number of accidental coincidences. Hence, signal-to-noise ratios must be kept large, and resolving times small.

Most of the conventional particle counters have been used successfully with synchrotrons. The Geiger counter, because of its relatively slow response and long recovery time has had but limited usefulness. It has been used in a few instances where signal-to-noise ratios have been made very large. Pulse ion chambers and proportional counters, while not suffering from the long recovery-time difficulties of the Geiger counter generally have relatively slow response times, and so have not been used nearly as much as the scintillation counter. Current scintillation materials and modern electronic techniques have permitted the use of resolving times down to $\backsim 5 \times 10^{-9}$ sec.

The pulse type operation of the synchrotron can be taken advantage of in at least one special detection method. As discussed in an earlier section (see p. 193), the burst of radiation can be made as short as 1 μsec. Hence, electrons arising from the decay of those μ-mesons ($\tau = 2.15$ μsec.) produced (either directly or indirectly) during the synchrotron burst will be in evidence immediately afterwards. Proper detection of these electrons can then be used to study the properties of the produced mesons.

Photodisintegration Experiments with a 300-M.e.v. Synchrotron

The x-ray beam of a synchrotron contains photons of all energies up to the operating energy of the machine. Not all of these photons, however, are equally effective in producing photodisintegrations. It has, in fact, been found that photons of energies near 20 M.e.v. are those most easily captured by nuclei (5a, 64a). Experimental investigations of the nuclear disintegrations produced by such photons have been carried out mainly with 20-M.e.v. betatrons and other "low energy" machines. This is partially because they can produce somewhat greater fluxes of 15 to 20 M.e.v. photons than a 300-M.e.v. synchrotron.

However, there are a number of interesting problems in nuclear photodisintegration that specifically require the use of a high energy machine. The interaction of a high energy photon with a nucleus can result in the ejection of two high energy nucleons or perhaps in the ejection of a number of nucleons with lower energies. Some work has been done on both these problems (73, 76a) but a number of questions need more investigation. It would be interesting to measure the probabilities for the emission of different possible nuclear fragments and the energy and angular distributions of these fragments.

Suppose one were interested in some disintegration involving the emission of several nucleons, say (γ, np) in a medium weight nucleus. Does a synchrotron provide enough intensity for an experiment involving such a process?

It is not hard to do a rough order-of-magnitude calculation. Assume that the target is placed in the synchrotron beam so as to intercept the entire beam. Then the yield of the particular "multiple" photodisintegration would be $n \cdot t \int (k/E) \cdot \sigma dE$ if we assume a $1/E$ spectrum; k measures the beam strength and n is the number of target nuclei/cm.^{3} and t is the thickness in centimeters; σ is the (γ, np) cross section of the target nucleus. Let us assume that the final nucleus is radioactive, and that it is possible to do chemistry to concentrate the activity. Because the photons are very penetrating, t can be fairly large. Say $nt \backsim 10^{23}$. Then the number of events excited in a target per second is of the order $10^{23}(k/E_m)\int \sigma dE$ where E_m is a mean energy for the photodisintegration. A reasonable estimate for $\int \sigma dE$ for a simple multiple disintegration in a medium weight nucleus is 1/10 M.e.v. barn (73a). This gives $\backsim (k/E_m)10^{-2}$ events per sec. If E_m is $\backsim 50$ M.e.v. and we want $\backsim 500$ events produced in the target per sec., $k \approx 2 \times 10^6$.

Now the total energy emitted in the beam per second is $\int_0^{E_e} (k/E) \cdot E \cdot dE$ or $k \cdot E_e$ where E_e is the synchrotron operating energy. If E_e is 300 M.e.v., we should want a beam energy of $\backsim 6 \times 10^{14} ev/s$. This is $\backsim 5 \times 10^2$ ergs/sec. in the beam. The Massachusetts Institute of Technology 200-M.e.v. synchrotron, as an example, is run at $\sim 5 \times 10^4$ ergs/sec. This leaves a margin of $\backsim 100$, but the calculation was perhaps a bit optimistic (assuming 100 per cent isotopic constitution; 100 per cent chemical recovery; activation to saturation, etc.); so that the intensity may not be ample but is probably adequate to permit a much more thorough investigation of high-energy photodisintegrations than has so far been possible.

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HIGH ENERGY ACCELERATORS

LINEAR ACCELERATORS[1,2]

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PRINCIPAL CONSTRUCTION PROJECTS

Linear accelerator design is still so new that it is far from standardized; every one of the some half dozen major construction projects is dealing with a machine different in some essential features from the others. For that reason this review will have to describe the nature of each machine, as well as consider their respective states of completion. For preliminary orientation, we list the projects which we shall discuss, with their main features.

At the University of California at Berkeley is Alvarez's original accelerator. This accelerates protons, injected at 4 M.e.v. from a Van de Graaff generator, to 32 M.e.v. The length of the accelerator is about 40 ft.; the radio-frequency (*rf.*) field inside it is in the form of a standing wave, and power is provided by 28 synchronized self-excited oscillators, closely coupled to the resonant cavity forming the accelerator, and operating at a frequency of approximately 200 megacycles per sec. This accelerator has been in operation for over two years, and during 1950 it was being used very successfully for nuclear research, notably proton-proton scattering, inelastic scattering of protons for energy level work, and work on short-lived isotopes. In addition, bombardments have been carried out for the chemistry and biology groups at Berkeley.

This Berkeley accelerator has proved to be such a useful tool for nuclear research that a similar but larger one is under construction at the University of Minnesota, under the direction of Professor John H. Williams. This also is for the acceleration of protons and is designed for a voltage of 66 M.e.v. To avoid the use of a Van de Graaff generator, initial injection will be at 500 k.e.v. from a transformer-driven source. The main acceleration will be pro-

[1] This review is essentially a survey of papers published in 1950.

[2] Two review articles on linear accelerators provide most of the background necessary for understanding their theory and design: "The Design of Linear Accelerators" by Slater (1) and "Linear Accelerators" by Fry & Walkinshaw (2). Both of these articles contain fairly extensive bibliographies, and between them they cover most of the necessary references. A recent reference not contained in either is "High Energy Accelerators at the University of California Radiation Laboratory" by Chew & Moyer (3). The theory of the linear accelerator is treated by Slater (4). Unfortunately, most of the recent information about the various projects is available only in progress reports and by private correspondence; the writer is indebted to representatives of the various projects mentioned for considerable information not available in the literature.

duced by three sections, each similar in a general way to the Berkeley accelerator, the first 20 ft. long, the other two each 40 ft. long. To simplify the problem of synchronizing these three sections, they will be fed by resnatrons operating as power amplifiers fed from a common crystal-controlled source. The Minnesota accelerator is in a relatively early stage, design having been completed and construction of the main components being under way.

The other projects are all concerned with electron accelerators. At Stanford the project initiated by the late Professor W. W. Hansen is proceeding in a developmental stage. This is a traveling wave accelerator, fed by high-power klystrons of a new design used as power amplifiers. The first efforts of the project were aimed toward the design of a suitable iris-loaded wave guide, slowing down the velocity of the traveling wave in the guide to the velocity of light, so that it would synchronize with the motion of the electrons (which after the first 2 M.e.v. are traveling with substantially the velocity of light). Such an accelerator, 12 ft. long and driven by a magnetron oscillator of frequency about 3,000 megacycles per sec., has produced 6 M.e.v. electrons. The more recent efforts have been largely headed toward the klystron design, and a klystron has been operated into an accelerator 12 ft. long, with an injected power of 8.5 megawatts in a 2-μ sec. pulse, producing an electron beam with a peak energy of about 35 M.e.v., with a maximum in the energy spectrum at about 30 M.e.v., and half amplitude at about ± 3 M.e.v. The klystrons are capable of delivering 14 megawatts in a 1-μsec. pulse, and an output power of 17 megawatts per klystron is anticipated for eventual operation.

In addition to these two working machines, the Stanford group is building a long accelerator which will ultimately be 220 ft. long and will be fed every 10 ft. by a klystron. With the measured characteristics of the accelerator sections, and an *rf.* power of 17 megawatts per klystron, this should give 45 M.e.v. per 10 ft., or 1,000 M.e.v. for the 220 ft. The accelerator will actually consist of 22 10-ft. sections, decoupled as far as the *rf.* is concerned, with a common electron beam traversing all of them, the phasing being controlled by driving all the klystrons from a common source. A length of 80 ft. of this projected 220-ft. accelerator is far along in its construction.

The Massachusetts Institute of Technology (MIT) accelerator, like the Stanford one, accelerates electrons in an iris-loaded guide. It is approximately 21 ft. long, and accelerates electrons injected at 2 M.e.v. from a Van de Graaff generator to about 17 M.e.v. Unlike the Stanford accelerator, but like the Berkeley one, it is a standing wave device. It is fed by 21 tunable magnetrons, with frequency of approximately 3,000 megacycles per sec., synchronized to each other and to the cavity. It consists of seven sections, each about 3 ft. long and fed by three magnetrons, decoupled from each other as far as *rf.* is concerned, but with a common electron beam. It has been in operation during most of 1950, and preparations are being made to use it for nuclear research. There are no plans for a larger accelerator of just this type.

The Atomic Energy Research Establishment in England has had an accelerator in operation for several years at the Telecommunications Research Establishment at Malvern, under the direction of D. W. Fry and associates. This, like the original Stanford accelerator, is a traveling wave electron accelerator, fed by a single magnetron. It is about 2 m. long and produces an electron beam of about 3.4 M.e.v., injection being from a 45 k.e.v. electron gun. One feature of the English program has been the very large currents which they have accelerated, of the order of magnitude of 100 m. amp. peak.

The British, particularly under the stimulus of Dr. G. R. Newbery at the Radiotherapeutic Research Unit of the Medical Research Council at the Hammersmith Hospital, have been actively pushing the use of linear accelerators for medical purposes. As part of this program, the Metropolitan-Vickers Electrical Co., Ltd., is starting to manufacture two types of linear accelerators for medical purposes. One type, being manufactured both by them and by the Philips Electrical Co., Ltd., is designed for 4-M.e.v. electrons. It is a traveling wave accelerator, 1 m. long, fed by a magnetron of 1.8 megawatts peak power at 3,000 megacycles per sec., using feedback. The other type, a longer accelerator fed by the same type of magnetron, is designed to produce 10 M.e.v. electrons. Both types of accelerators will be designed specifically for medical use, being conveniently adapted for treating patients. It is understood that these machines are under construction, but not yet in operation.

At Purdue University, under Professor F. F. Rieke, there has been under way for some time a project for making an electron accelerator powered by magnetrons of 3,000 megacycles per sec. The first version of this accelerator was a traveling wave iris-loaded tube much like that at Stanford, fed with one magnetron, accelerating electrons injected at 300 k.e.v. from a Van de Graaff generator to an energy something over 1 M.e.v. A new accelerator now under construction will consist of two parts fed from a common source of power, consisting of several magnetrons phased together and stabilized by means of a stabilizing cavity. Each of the two parts will be a traveling-wave section, and the accelerator is being designed for the 5 to 10 M.e.v. range.

At Yale University, Professor H. L. Schultz and associates are constructing an electron accelerator consisting of a number of separate accelerating cavities, each excited by a triode power amplifier fed from a common source. It operates at 580 megacycles per sec. With seven sections operating, an electron energy of approximately 4 M.e.v. has been obtained. Development of the power sources is proceeding.

Design Similarities and Differences

Now that we have considered the principal construction projects, let us take up some of the main features of resemblance and difference between the various designs. First, we note the rather fundamental difference between the proton accelerators on the one hand and the electron accelerators on the other. A proton accelerator is dealing with particles moving much more

slowly than the velocity of light, so that we meet the problem of slowing down a wave in a guide to a very low velocity. This cannot be accomplished conveniently in the iris-loaded guide; instead, the type of construction indicated is that used in the Berkeley and Minnesota accelerators, in which the protons pass through a series of hollow drift tubes inside a larger cylindrical cavity, being acclerated at the gaps between drift tubes and being protected inside the drift tube when the *rf.* field is in the opposite phase, in which they would be decelerated if they were in the gaps. Geometry shows that if frequencies as high as those in the microwave region are used, the drift tubes become too small in diameter to allow the passage of the beam; to make them conveniently large, a much longer wave length and lower frequency must be used, leading to the choice of approximately 200 megacycles per sec. for this machine. The mode of oscillation in which it is operated is inherently a standing wave mode, so that the question whether to use a standing or traveling wave does not arise. We thus are led to the main features of the design of the proton accelerator, in a straightforward manner.

One aspect of its performance follows directly from its design: the drift tubes must be so constructed as to prescribe the speed of the protons at each point of the accelerator, since the protons must go from one gap to the next in one period of the *rf.* field. Thus the final energy of the protons is so-to-speak built into the machine, and the protons are bound to come out with this speed, so long as enough accelerating field is provided by the oscillators. This reduces somewhat the flexibility of the accelerator: there is no adjustment by which the energy of the ions can be changed. This is being circumvented in the Minnesota design by making the accelerator in three sections, of which one, two, or all three can be operated, producing three possible energies. There is a compensating advantage, however: the emerging protons have a rather narrow spectrum of energies, since a proton with the wrong energy has the wrong velocity and soon gets lost from the accelerating beam. Another aspect of performance is also a result of the design. A cavity as large as that used in the Berkeley accelerator, at such a comparatively low frequency, has a very high Q, and requires a long time to have its power level build up. It is worth while, then, to operate it with a long pulse length. Thus it comes about that the proton accelerators operate during each pulse for about 300 μsec., a feature of great value in nuclear experiments using coincidence methods, since it is well known that the number of accidental coincidences in a pulsed machine is inversely proportional to the on-time.

In contrast to the proton accelerators, the speed of an electron approaches the speed of light very closely at energies above 2 M.e.v. and is not very far below, even at the lowest injection energies used for any of the electron accelerators. As a consequence, the iris-loaded wave guide can be used, and all the electron accelerators except that of the Yale project use guides of similar nature. This guide has a large hole down the center for passage of the beam, even when constructed for microwave frequencies, and this proves to be advantageous from the standpoint of power consumption and power storage.

It thus comes about that all electron accelerators are operated at high frequencies, all at about 3,000 megacycles per sec. except for the Yale accelerator. As a corollary, the build-up time of the cavities is small, of the order of 2 μsec., and the on-time of the beam is likewise small, generally about 1 μsec. This is a disadvantage as far as use of coincidence methods is concerned, as we mentioned earlier; but it may be a compensating advantage in certain other types of work, such as study of nuclear reactions with fast time-constants or the production of short pulses of neutrons for a velocity-selector, where the short pulse lengths can be used to advantage.

Another result of the nature of electron accelerators is that, since they operate for most of their length at the velocity of light, an electron remains in step with the field over a considerable range of phase differences: if it is in the most advantageous phase, it picks up a maximum amount of energy; but in a somewhat different phase, though it gains less energy, it still remains at approximately the velocity of light. Thus the energy of the emergent beam is not a design feature of the machine, as it is with the proton accelerator. As a result, the energy of the electrons can be easily regulated by varying the power fed into the accelerator, a useful feature for flexibility. On the other hand, electrons with a wide range of energies can get through the accelerator, so that the final beam is not as nearly monoenergetic as with the proton accelerator.

One of the most important technical differences between the various accelerators is in the way of feeding in the power. The English accelerators use only a single magnetron, as did the original Stanford and Purdue accelerators. This is practicable for the English accelerator, for there is available in England a magnetron capable of producing approximately two megawatts, which is enough to feed a rather powerful accelerator. Such a high powered magnetron was not available in the United States at the time the accelerator projects were started, so that any project looking forward to a high energy beam had to think of operating with a number of separate power sources. These could be either magnetrons operated as self-excited oscillators (which was practicable since there were available in this country moderately high-power tunable magnetrons), self-excited oscillators of lower frequency (as in the Berkeley accelerator), or power amplifiers (as the resnatrons in the Minnesota accelerator, triodes in the Yale accelerator, and klystrons in the Stanford accelerator). It thus has come about that the American developments are more in the direction of accelerators fed by many power sources, which therefore are inherently capable of being extended to very high energies, whereas the British development is limited to some 10 M.e.v., the practical limit attainable with one of their magnetrons (since it is not feasible to synchronize the nontunable British magnetrons).

The problem of synchronizing many power sources is obviously a difficult one, and one that must be solved with great perfection in order that they may remain in phase during the whole of a pulse. The simplest way to do this is obviously by using the sources as power amplifiers, feeding them all from a

common signal which can be controlled by crystal or other means to tune it to the desired frequency. The resnatron as proposed at Minnesota, and the klystron at Stanford, seem to be the ideal methods of feeding power into such a device, and it is to be expected that future linear accelerator designs will make use of such power amplifiers. To avoid the complications of electrical coupling between the various amplifiers, the designs will presumably, as at Minnesota and Stanford, subdivide the accelerator into a number of electrically independent sections, one fed by each amplifier. An adjustable phase delay in the line leading from the common signal to each section then will permit adjusting the relative phases of the sections so that an ion or electron emerging from one will find itself in the correct phase of the field in the next section.

The use of such power amplifiers is not the only way of achieving synchronization, however, as is shown by the Berkeley and MIT accelerators, which operate with self-excited oscillators, triodes at Berkeley and magnetrons at MIT. The reason why such operation is possible is that a relatively small phasing signal fed into a self-excited oscillator, provided its frequency is very close to that to which the oscillator is tuned, can control both the frequency and phase of the oscillator and hence effectively convert it into an amplifier, though one with an extremely small frequency range in which it works, but with correspondingly great gain. Self-excited oscillators rather than power amplifiers were used in these two projects largely for reasons which no longer apply: when the projects were started, they were more available than power amplifiers, particularly in the microwave region, where the Stanford high-power klystron project had not been undertaken at the time the MIT accelerator was designed.

To synchronize self-excited oscillators, they must be tuned together with great accuracy, since the phasing signal can pull their frequency only over a very narrow frequency range; and this demands more accurate tuning than can be accomplished or maintained without special means. The easiest way to stabilize the frequency of a self-excited oscillator is to couple it into a resonant cavity of high Q, which, in effect, reflects back a signal whose frequency is the resonant frequency of the cavity; this signal then operating as a phasing signal for the oscillator. This would not be necessary if the tank circuit of the oscillator (that is, the resonant cavity of the magnetron) had a sufficiently high Q, but ordinary oscillators are not made with very high Q circuits. The natural thing to do in setting up a synchronizing system for a linear accelerator is then to use the accelerator itself as the stabilizing cavity, which means operating it in a resonant mode, or with a standing wave, rather than with a traveling wave. It is for this reason that the Berkeley and MIT accelerators both operate with standing waves (though as we have pointed out this is the natural type of mode to use for the proton accelerator). The projected Purdue accelerator will, however, use a separate stabilizing cavity and will use traveling wave operation of the accelerator.

A number of oscillators can be stabilized by the same stabilizing cavity.

In the Berkeley accelerator, all 28 oscillators feed into the single resonant cavity, the signal returning from it regulating the frequency and phase of all oscillators. In the MIT accelerator three magnetrons feed into each resonant cavity. It is natural that, with a number of oscillators feeding into a single cavity, there should be a confusion of phase while the pulse starts, when they are trying to establish synchronism. This is obviated by prepulsing certain oscillators, letting them determine the phase for the others. In the MIT accelerator, there is then the problem of synchronizing all seven electrically decoupled sections. They are tuned accurately to the same frequency and are started in phase by prepulsing one section, feeding a phasing signal from it into each of the other six, and forcing the others to start in a definite phase relation by this phasing signal, which then plays the role of the input signal in the accelerators that operate with power amplifiers. As in those accelerators, adjustable phase delays are introduced into the phasing lines from the master section to the others, so that the phase as well as the frequency of each section can be regulated.

There is a considerable sacrifice in power in operating a self-excited oscillator into a resonant cavity, as contrasted with operating a power amplifier into a nonresonant cavity. The tank circuit of a self-excited oscillator can perform coupled oscillations with the resonant cavity, and this results in two modes of operation, one throwing most of the power into the cavity, the other into the oscillator itself; unfortunately, the second mode, which does not contribute to building up the oscillations in the cavity, is the one which normally starts. To avoid this, a resistive load must be introduced into the system, resulting in considerable loss of power. This is partly obviated in the Berkeley accelerator, where it has been found possible to introduce resistance only into the prepulsing oscillators, the others being closely coupled; but a corresponding method has not so far been found possible in the MIT accelerator, where magnetrons are harder to deal with than comparatively low-frequency triodes. In addition, the MIT accelerator suffers somewhat in power by using a standing wave rather than a traveling wave, as is necessitated by using the accelerator itself as a stabilizing cavity; the standing wave consists of two traveling waves, one in each direction, only one of which is effective in accelerating electrons, while both dissipate power. It is for these two reasons that the MIT accelerator appears to get less acceleration per magnetron than the projects using traveling waves; and it is for reasons like this that future accelerators will presumably use power amplifiers, now that they are available.

One feature in which all linear accelerators are potentially valuable is in the possibility of using a high beam current, with of course the possibility of having this beam emerge in a well-collimated and usable form. The beam current in the proton accelerators is of course limited by the ion source; the Berkeley accelerator had some time ago a peak current of the order of 1 μamp. with an average current of the order of 4×10^{-9} amp., though later work has increased the beam current. The electron accelerators have much

higher current, however, since it is comparatively easy to get high electron emission, and it is to be expected that they can far surpass betatrons and synchrotrons in their currents, so that when they have attained the same beam energies, they should be by far the most powerful electron accelerators. The English experimenters, as has been mentioned, have been more active than other groups in increasing their beam currents, but there is no reason why the other electron accelerator projects cannot attain similar currents. The beam current can be made large enough so that a considerable fraction of the power fed into the accelerator reappears as energy of the accelerated electrons rather than being dissipated in the resistance of the walls; the British accelerator has operated at efficiencies as high as 36 per cent (that is, 36 per cent of the incoming energy appears as beam energy). It is not desirable to attain such high efficiency, however, since as more power flows into the electrons, the loaded Q of the cavity decreases and the voltage does not build up to its maximum value. The British have been able to load their accelerator so heavily that the voltage fell far below the maximum attainable value. Even with this limitation, however, very high currents are possible. Simple calculations show that if something like 10 per cent of the energy is absorbed in the beam, with the various accelerator designs proposed, the resulting peak current will be of the order of 50 to 100 ma.

The discussion which we have given should suffice to show the differences as well as the resemblances between the various accelerator projects and to indicate the probable lines of development in the future. We may look particularly for an extension of the Stanford type of design, a traveling-wave accelerator made up of a number of sections each fed by a power amplifier, accelerating electron beams with peak currents of a good many milliamperes, in pulses of the order of a microsecond. There is no clear limit as to the possible acceleration to be attained by such a machine; experience so far has indicated that it is not hard to get a well-collimated beam down a fairly long accelerator.

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DETECTION OF NUCLEAR PARTICLES

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Introduction

This chapter will be concerned primarily with the techniques for detecting and measuring the energy of individual particles and quanta. The emphasis will be on the developments that have occurred during the past year; the majority of references are to papers published during 1950. In order to present a coherent story, the earlier work has been briefly summarized, usually without references to the authors responsible for the developments. Goldsmith (10) has published an excellent bibliography of the major papers through 1948. Since that time several excellent books on radiation detectors have been published. Rossi & Staub (17) have described the intensive work on ionization chambers and proportional counters that was carried on at Los Alamos during the war. Curran & Craggs' monograph *Counting Tubes, Theory and Application* (6), is of broader scope; these authors discuss the various detectors and circuits and how they are used in nuclear research. Certainly the most complete and authoritative work on the physics of ionization chambers, proportional counters, and Geiger counters thus far published appears in a recent book by Wilkinson (24).

One of the best review articles on radiation detectors has been written by Corson & Wilson (5). An expanded and more recent version (26) of this paper is scheduled for publication. Some of the material in this chapter of necessity parallels that of the above mentioned review, to which the reader is referred for a more complete presentation.

Space limitations have, at least in part, limited the scope of this chapter. The vast field of Geiger counters has been neglected. No mention is made of electron multipliers for heavy particle detection; a good review has recently been written by Allen (1). Crystal counters have not been touched upon, chiefly because scintillation counters have, in a large measure, replaced them as particle detectors. The inherently better energy resolution of crystal counters has not been realized, and the experimental difficulties in their use are formidable. Hofstadter (12) has reviewed the subject of crystal counters. The use of photographic emulsions for the study of nuclear particles has been mentioned only in connection with neutron and γ-ray spectroscopy. The author does not feel competent to do justice to the many powerful applications of this technique. A recent book, *Progress in Nuclear Physics*, Volume I, has a chapter devoted to photographic emulsions (9).

The successful operation of the detectors described in this chapter depends on having dependable electronic equipment connected to them. The importance of this factor cannot be overemphasized. However, so large a subject would certainly be outside the scope of this chapter, and the reader is

referred to Elmore's excellent book (7) for circuits suitable for the various applications.

There have been some very significant advances in particle detection within the past few years, for example, the use of electron collection in ionization chambers and counters, the development of the β-proportional counter, and the use of solid ionization media in crystal counters and scintillation counters. These advances have resulted in a considerable increase in the speed of response; particle energies can be measured over a much wider range; recovery times are greatly reduced; and the sensitivity for γ-radiation has been increased many fold. These advantages can mean a great deal to the experimenter as can be seen from a brief consideration of each.

Fast response.—A Geiger or proportional counter exhibits a considerable and variable delay between the passage of the primary particle and the generation of the pulse. Such delays cannot be tolerated if one is trying to measure a half life of a few millimicroseconds. Fast response is needed to measure the time of flight of a fission fragment or an annihilation γ-ray. It is also of great value in coincidence work for it allows one to reduce the coincidence resolving time, thereby reducing the number of accidental coincidences which, in some circumstances, may obscure the real coincidences. Scintillation counters have proven particularly useful when fast response is required.

Fast recovery.—Not only should a detector respond quickly to the passage of a particle, but it should also recover and be ready to respond to the next particle within as short a time as possible, otherwise the counting rate is seriously limited. This problem is particularly pointed up when pulsed accelerators are used to generate the particles to be detected. Although the average counting rate may be low, the counting rate during the few microseconds duration of the pulse may be very high. In coincidence experiments, it is frequently necessary to deal with very high counting rates in a given detector in order to get a coincidence rate of a few counts per minute. A similar situation occurs when one is exploring a pulse height distribution with a single channel analyzer having a narrow channel width.

Pulse height proportionality.—There are many situations in which it is advantageous to use a detector that delivers a pulse whose height is proportional to the energy of the primary particle. Such a detector can, of course, be used to measure the energy of the particle. Although the energy resolution of present day detectors is rather poor compared to that of a magnetic spectrometer, this disadvantage may be outweighed by the high detection efficiency.

Energy sensitive detectors are very useful for decreasing the background when one wishes to count particles of a given total energy or a known specific ionization. For example, the particle detector in a magnetic spectrometer may be set to count only those particles that satisfy the magnetic field conditions, or the counters in a cosmic ray telescope can be set to trigger on only those particles that penetrate the counter with a given loss in energy in the counter. The development of the β-proportional counter has extended the low energy

range of such detectors; the use of counters with solid ionizing media have extended the high energy range by perhaps a hundred fold.

One frequently encounters the problem of counting heavy particles (e.g., α or proton) in the presence of an intense background of γ-radiation. In such a case the detector dimensions can be chosen such that the heavy particles give much larger pulses than the electrons from the γ-rays. It is further necessary to use a detector with quick recovery time so that the pulses from the electrons do not overlap and thus build up to a large pulse.

Efficiency.—While most detectors have a high efficiency for detection of particles passing through them, problems of source thickness and extent, solid angle, etc., will determine the choice of the best counter for the purpose. This is particularly true when one wishes to detect γ-rays or neutrons; since such radiation is detected only by its interaction with matter, it is obviously important to use a counter with a considerable mass of sensitive material. Scintillation counters have been especially valuable in this respect. The need for high sensitivity becomes apparent when one tries to measure the energy spectrum of the γ-rays from a weak source. Even with a large NaI crystal, the counting rate in a single channel may be only 0.1 count per second so that long counting times are required to get good statistical accuracy.

Scintillation Counters

Although relatively new, scintillation counters have assumed an important place in the field of particle detectors. They can be used to measure particle energies from a few thousand electron volts well up into the million electron volt region. Resolving times less than 10^{-8} sec. are obtainable; indeed, metastable states with decay times shorter than 10^{-9} sec. have been measured by coincident scintillation counters. (65). These features, plus the high efficiency for γ-ray detection, have made these counters exceedingly useful in many fields of nuclear physics. The state of the art of scintillation counting was reviewed by Jordan & Bell in 1949 (58). Most of what follows will be concerned with improvements since that date.

Simple radiation detectors have been made by placing a scintillation phosphor in close proximity to a photomultiplier tube and observing the average current collected at the last dynode; however, the sensitivity is severely limited by the "dark current" of the tube. Considerable improvement can be obtained by following the photomultiplier with a cathode follower and a biased diode rectifier. Kallman has detected a 1-mc. radium source at a distance of 10 m. with such an arrangment. For most applications, one wishes to count the number and size of the light flashes produced by the passage of individual particles through the phosphor. This is conveniently done by connecting the photomultiplier collector to the input grid of a linear amplifier.[1] This in turn feeds into a pulse height analyzer or coincidence detector.

[1] It is occasionally convenient to obtain positive pulses from the dynode preceding the collector.

Figure of merit.—If one desires to get the best possible energy resolution, the following items are of importance: (*a*) a phosphor must be selected with a high efficiency for conversion of particle energy to light energy; (*b*) as large a fraction as possible of the light emitted should be channeled onto the photocathode of the multiplier; (*c*) the photomultiplier tube should have an efficient cathode for converting the light to photoelectrons; these photoelectrons should all be focussed on the first dynode and amplified proportionally in the following stages. These three efficiencies can be grouped together to give an over-all figure of merit for the system, sometimes expressed as the ratio of the amount of energy lost by the particle to the number of photoelectrons collected; this number is usually given in kilo electron volts per photoelectron.

Measurements of the over-all figures of merit have been made by Hopkins (53) by two methods. The first was suggested by Morton (67) and involves the measurement of the average pulse height due to a single photoelectron from the multiplier cathode. Then the pulse height produced by an electron of known energy traversing the phosphor is measured. Thus one obtains the number of photoelectrons produced by a β-particle of known energy.

The second method used by Hopkins is based on the assumption that the observed distribution in pulse heights, produced by a monoenergetic β-ray source, is due to statistical fluctuations in the number N of photoelectrons produced, plus any further smearing due to the secondary multiplication of the dynodes. Electrons of known energy E falling on the phosphor will produce pulses from the photomultiplier and amplifier. If one measures the number of pulses (per unit time) for each setting of the pulse height analyzer, there will be a single sharp peak in the number versus energy curve. The position of this peak allows one to calibrate the analyzer dial in energy units. The shape of the peak is approximately gaussian so that if the half width of the peak (at $1/e$ of maximum) is a energy units wide, the root mean square deviation is $a/\sqrt{2}$ and the relative deviation $a/\sqrt{2}E$. Setting this equal to the expected relative deviation in N, the number of photoelectrons, one obtains

$$\frac{1}{N^{1/2}} = \frac{a}{\sqrt{2}\,E} \qquad 1.$$

or

$$\frac{E}{N} = \frac{a^2}{2E}. \qquad 2.$$

The term on the left is the figure of merit defined previously. Morton has shown (67) that multiplier statistics, chiefly because of the first dynode, increase the fluctuation by an amount $r/(r-1)$ where r is the secondary emission ratio. Thus equation 2 should be modified to read

$$\frac{E}{N} = \frac{a^2}{2E} \cdot \frac{r-1}{r}. \qquad 3.$$

Hopkins measured E/N for an anthracene crystal cemented to a 5819 photomultiplier by both methods and found a value of 2 k.e.v. per photoelectron, independent of the β-ray energy. A better tube gave a value of 1.4. Hofstadter *et al.* have measured the figure of merit with NaI crystals and find values between 0.66 and 1.0 k.e.v. per photoelectron (51, 77), the better values being obtained when low voltage x-rays were used for a radiation source. At Oak Ridge National Laboratory, the resolution obtained with Cs^{137} γ-rays is, at present, about 9 per cent full width at half maximum; when this value is used to calculate E/N by equation 3, a figure of 0.73 k.e.v. per photoelectron is obtained. Pringle & Standil (71) obtain a value of 1.5 when a NaI crystal is used on an EMI5311 photomultiplier tube.

Phosphor efficiency.—The above measurements allow a rough calculation of the phosphor efficiency. If one assumes that all of the light from the phosphor is collected on the photocathode, which in turn converts 10 per cent of the photons into photoelectrons, then some 100 e.v. are required to produce one photon. Assuming an average of 2.7 e.v. per photon, the conversion efficiency of anthracene and sodium iodide is roughly 2.7 per cent. Hopkins also compared the pulse height of α-particles on a ZnS-Ag phosphor with electrons on anthracene and deduced that the efficiencies were nearly equal. This is at variance with the earlier work of Kallman (59); he measured efficiencies of some 25 per cent.

It is well known that the conversion efficiency of the organic phosphors is much lower for α-particles than for β-particles. This effect has been investigated by Franzen *et al.* (43) and by Birks (39). The latter finds that the number of photons emitted, when anthracene is bombarded with α-particles, is proportional to the range of the particle in the crystal rather than to the energy dissipated. So long as the particle loses energy at a rate less than 0.005 M.e.v. per cm. of air, the amount of light is proportional to the energy of the particle. (This corresponds to a β-particle of energy greater than 100 k.e.v.) When the energy density exceeds 1 M.e.v. per cm. of air (a 5 M.e.v. or slower α-particle) the amount of light is proportional to the track length. This is explained on the basis that some 10 e.v. of energy is lost per molecule encountered which is sufficient to break the chemical bonds (37).

Hopkins (53) has measured the relation between pulse size and electron energy loss in anthracene and finds it to be linear above 125 k.e.v., the departure at low energies apparently being due to the too great ionization density.

The inorganic phosphors are less affected by ionization density and hence perform much better when used for α-particle measurements. On the other hand Kruger (63) reports that 11 M.e.v. deuterons give 2.2 times as large a pulse in NaI(Tl) as 11 M.e.v. α-particles. (The ratio with anthracene was 4 to 1.) Pringle & Standil (71) have plotted pulse height versus γ-energy absorbed in NaI(Tl) and found almost the same relationship that Hopkins observed in anthracene; the lack of linearity below 125 k.e.v. must be ascribed to too great an ionization density.

Many solid phosphors have been discovered which scintillate when bombarded with charged particles. Table I, taken from Hofstadter (48), lists general properties of some of the more useful ones. Of these, only three or four are widely used. Anthracene, which is now available commercially, has the highest efficiency for conversion of β-particle energy into light energy of any of the organic phosphors. The decay time is short and the surfaces are stable when exposed to the atmosphere. Stilbene is occasionally used when very short resolving times are required although its efficiency is poorer than anthracene. *p*-Terphenyl has somewhat similar properties to stilbene and good crystals are readily grown. NaI(Tl) crystals are now in general use for γ-ray detection. The crystals are hygroscopic and hence must be covered, which limits their use for β-ray measurements. Their high efficiency for light conversion and the relatively high density and atomic number are of great value for detecting and measuring weak γ-ray sources.

Solution phosphors.—It has recently been discovered that many organic phosphors still scintillate when dissolved in various solvents (60, 74). Although the light conversion efficiency is less than for the pure solid phosphor, the amount of light emitted is considerably larger than would be expected from the fairly low concentration of dissolved phosphor. For example, a solution of 5 gm. per l. of terpheynl in *m*-xylene produces pulses about half as large as solid terphenyl. As the concentration of phosphor in the solution is increased, the amount of light increases proportionally for small concentrations, passes through a maximum, and then decreases for large concentration. Kallman (61) explains this as follows: The energy from the original ionizing event is first absorbed by the solvent molecules; this energy is then transferred to the fluorescent molecules where it is trapped until radiated in the form of light; this process is in competition with other processes which do not produce light.

Solution phosphors have two advantages. First, the decay time for the light flash is very short; 2×10^{-9} sec. has been observed in one instance. Second, one can easily make phosphors of any size and shape without the attendant difficulties of crystal growing. This last factor may be of considerable value in cosmic ray research where large volumes of phosphor are required. An interesting type of solution phosphor has recently been reported (75). A solid solution of terphenyl in polystyrene scintillates although the pulses are quite small.

Light collection.—As previously mentioned, in order to detect low energy particles and get good energy resultion of fast particles, it is necessary to collect nearly all the light from the phosphor onto the photocathode of the multiplier. With 1P21 type tubes this is impossible because of the location of the photocathode. In the newer type tubes, such as the RCA 5819 and the EMI 5311, the cathode is coated on the inside of the glass envolope as shown in Figure 1. Usually the phosphor is attached to the tube face with Canada balsam or a film of mineral oil. This minimizes reflection at the lower surface of the crystal by providing a nearly constant index of refraction between

phosphor and cathode. The crystal is then surrounded with a reflector which is not in optical contact with the crystal, thereby taking advantage of total reflection for light rays that strike at an angle greater than critical.

The best type of reflector has been a subject of some controversy. Most workers use an aluminum foil folded over the crystal and taped to the side of the tube. The problem becomes more difficult when the crystal is larger than the photomultiplier tube. With a 4-in. diameter crystal, for example, P. R. Bell uses a truncated lucite cone 3 in. long, 4 in. in diameter at the large end and $1\frac{1}{2}$ in. in diameter at the small end. The cone is optically connected to the tube and phosphor and closely surrounded with aluminum foil. He reports less than 50 per cent light loss with this arrangement. Batchelor *et al.* (32) have made experiments with cones, paraboloids, hemispheres, and spheres.

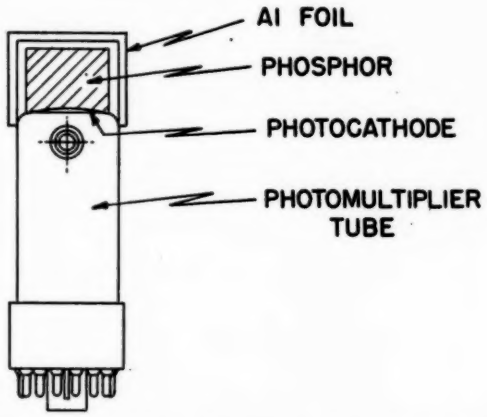

FIG. 1. One method of mounting a scintillation phosphor on a photomultiplier.

They found that an integrating sphere with a diffuse surface of magnesium oxide gave the best results. Bell and Davis have also compared integrating spheres and foil coverings and found the sphere slightly inferior; in either case it is important to cement the phosphor to the tube (1a).

The arrangment shown in Figure 1 suffers one disadvantage. Light which originates in the phosphor near the surface of the tube will illuminate that portion of the photocathode most strongly which lies just underneath the origin. Unless the cathode is uniformly sensitive over the face of the tube, the pulse height will depend on where the nuclear particle strikes the phosphor. Variations in cathode sensitivity of two to one are not uncommon, even for an otherwise good tube. This situation can be greatly improved by inserting a half-inch long cylinder of lucite between the phosphor and tube. A good grade of lucite must be used or the loss of light in it will offset the improvment in uniformity of illumination. Care should be taken not to use ultraviolet-absorbing lucite.

TABLE I

GENERAL PROPERTIES OF CRYSTALS††

Material	Emission spectrum Å	Absorption spectrum Å	Relative light yield‡ (Uncorrected) for β-particle	Decay constant¶ $\times 10^8$ sec.$^{-1}$	Response to monoenergetic particles			Light yield per M.e.v. for different particles**	Density gm./cm.^{3}	Melting point (°C.)	Miscellaneous
					Alpha	Beta	Proton				
Anthracene	4400 (60)*	Starts at ~4050	1.0	3.0 ± 0.5 (300°K.) 1.2 ± 0.2 (77°K.)	Nonlinear	Linear between 125–1900 k.e.v.	Nonlinear	$\beta/p\cong2.0$ $\beta/\alpha\cong8.0$	1.25	217	Good crystals rather hard to grow
Stilbene	4200 (weak) (360) 4080 (100) (strong)	Colorless	0.6	Between 0.6 and 1.2	—	—	—	Not constant	1.16	124	Good crystals readily obtained
Phenanthrene	4100 (100) 4300 (100)	Colorless	0.3	0.8	—	—	—	—	1.03	100	Extremely difficult to obtain clear crystals
Dibenzyl	3520 3710 3950 (weak)	Colorless	0.6	~1.6	—	—	—	—	1.00	52.5	Good crystals readily obtained
Terphenyl	3900 4050 4300	Colorless†	0.65	~1.2	—	—	—	$\beta/\alpha\cong8.0$	1.23	213	Good crystals readily obtained; Rugged
Naphthalene	3450 (250)	Colorless	0.25	~6.0	—	—	—	Not constant	1.15	80	Good crystals readily obtained; Sublimes

Material	Emission spectrum Å	Absorption spectrum Å	Relative light yield‡ (Uncorrected) for β-particle	Decay constant¶ $\times 10^8$ sec.$^{-1}$	Response to monoenergetic particles			Light yield per M.e.v. for different particles**	Density gm./cm.^{3}	Melting point (°C.)	Miscellaneous
					Alpha	Beta	Proton				
NaI(Tl)	4100 (800)	Colorless 2930 2340	~2.0	25	Approx. linear	Linear	Linear	$\beta/p=1.0$ $\beta/\alpha\cong 1.0$	3.67	651	Excellent crystals readily obtained; Hygroscopic
KI(Tl)	4100 (900)	Colorless 2870 2360	~0.5	>100	Approx. linear	Linear	Linear	$\beta/p=1.0$ $\beta/\alpha\cong 1.0$	3.13	582	Excellent crystals readily obtained
CaI(Tl)	White	Colorless	~1.5	>100	—	—	—	—	4.50	621	Excellent crystals readily obtained
LiI(Tl)	Blue Green	Colorless†	~1.0	>100	—	—	—	—	4.06	446	Very hygroscopic
$CdWO_4$	5200 Green	Yellow Starts at 4500	~2.0?	Long	—	—	—	—	7.90	1325	Good small crystals readily obtained
$CaWO_4$	4300 Blue	Colorless Starts at 4000	~1.0	Long	—	—	—	—	6.06	1535	Good small crystals readily obtained
ZnS(Ag)	Blue		~2.0	>1000 Decay not exponential	Approx. linear	—	—	$\beta/\alpha=1.0$	4.10	1850	Only powder or small crystals obtainable

* Number in parentheses is the bandwidth at half-maximum.
† Sample studied was slightly yellow.
‡ This is the integrated light yield, with anthracene considered to be 1.0. Values are uncorrected for response of photomultiplier (5819).
¶ τ, the decay constant, is that which appears in $e^{-t/\tau}$.
** Values are correct in the range of α and proton pulses of 5 M.e.v.
†† From a paper presented by Hofstadter at a meeting of the American Physical Society on April 1, 1950 (48).

Factors affecting resolution.—The loss in resolution due to poor statistics can only be improved by increasing the efficiency of conversion of particle energy into photoelectrons. On the other hand there are additional reasons for a spread in pulse height. Some may be electronic in nature, such as hum in the photo-tube supply voltage, or noise in the amplifiers. Variable magnetic fields at the photo-tube are particularly troublesome; working near a saturable reactor regulator is to be avoided.

Inhomogeneities in the phosphor will result in a large spread in pulse heights; however, a crystal with several cracks in it is still capable of giving good resolution. If the crystal is not completely transparent to its own luminescent radiation, then light flashes that originate near the photo-tube face will be more effective than light flashes coming from points further away. Measurements on the absorption spectrum of NaI(Tl) indicate that part of the emission spectrum near the ultraviolet end should be partially absorbed. In this event, the use of a properly designed light filter between the tube and crystal should improve the resolution. Experiments in progress by Bell have indicated that some improvement can be obtained with such a filter.

The proper treatment of the surface of NaI(Tl) crystals appears to have an important bearing on the resolution that can be obtained. The pulse height and resolution get poorer very rapidly if any water vapor becomes absorbed by the surface of the crystal. Moreover we have found that solution polishing is inferior to mechanical polishing; actually the best resolution is obtained by leaving the surfaces rough ground with 320 Carborundum.

Photomultiplier tubes.—The RCA 5819 and the EMI 5311 are in general use for scintillation counting. The cathode sensitivity has been improved during the past year; 40 μamp./lumen is an average value at present, although some tubes run as high as 60 μamp./lumen (50 μamp./lumen corresponds to an efficiency of one photoelectron for every 10 photons of 3 e.v. energy). The tubes are sensitive to magnetic fields, hence a mu-metal shield around the tube is recommended. The need for cooling the tube to reduce the noise of the tube has largely disappeared. Careful attention to phosphor and light collector will enable one to detect 20 k.e.v. electrons with essentially no noise counts. Although some 5,000 electrons/sec. are emitted from the photochathode of a 5819 tube at room temperature, a counting rate of only one per second will be observed if the bias is set at six "average electrons" (67). A 20-k.e.v. electron in the phosphor should produce some 15 photoelectrons and, hence, will have a high probability of being detected when the discriminator is set to trigger on pulses 6 electrons high.

As pointed out by Morton (67) part of the width of the distribution of pulses from monoenergetic electrons is due to the multiplier, namely the factor $r/r-1$ where r is the secondary multiplication ratio. Actually the first stage of the multiplier contributes most of the effect. It is, therefore, of some value to increase the voltage on the first few stages. For example Bell uses a 470,000-ohm resistor between the cathode and first dynode, a 150,000-ohm resistor between first and second dynode, and 100,000-ohm resistors

between succeeding dynodes. By applying 800 v. across the resistor string, the appropriate voltages at the dynode are obtained.

If one attempts to increase the total voltage across the multiplier to get a higher multiplication ratio and larger pulses, the noise increases greatly because of positive ion feedback. Post & Shiren (68) have successfully pulsed the multiplier to high voltage for a few microseconds; positive ion feedback does not take place during this short interval. Actually Allen & Engelder (27) have shown that it is sufficient to pulse only the fourth dynode; this makes the pulser simpler and avoids transients in the output dynode. This technique is particularly useful when used in conjunction with a pulsed cyclotron.

Experimental tubes with 12 stages have been built which give much larger pulses than the 5819 (10 stages). Other types of photomultiplier tubes are being investigated by Morton at the Radio Corporation of America. One is a tube with a 3-in. photocathode for use with large crystals. Experimental ultraviolet-sensitive tubes have already been built. Such tubes will permit a broader choice in the types of phosphors.

Applications—β-ray spectrometer.—If one wishes to measure the energy of nuclear particles with some precision, the components must be chosen carefully and assemblied properly. A typical scintillation spectrometer for measuring β-ray spectra might be built as follows. An anthracene crystal approximately 1 in. in diameter and $\frac{1}{4}$ in. thick is cemented to one end of a lucite cylinder, the other end being in turn cemented to a 5819 photomultiplier tube. A piece of 0.2 mil aluminum foil is used to cover the crystal except on the exposed end which is covered by 0.2 mg./cm.^{2} foil as a β-ray window. The entire assembly is then mounted inside a light tight metal can with suitable connectors for electrical leads; alternately one might mount the tube inside a lead "pig" to reduce the background.

The high voltage supply for the photomultiplier may either be batteries or an electronically regulated supply. The amount of hum or drift must be kept within 1/10 v. or less since the gain of the photomultiplier varies approximately as the seventh power of the applied voltage. It is good practice to monitor the voltage with a laboratory potentiometer by measuring the current in the divider string.

The pulses must be amplified by a good linear amplifier such as the Oak Ridge A-1 (57) or the Los Alamos Model 500 (41). While the A-1 has an integral pulse height selector, for accurate work a single or multi-channel analyzer should be used instead. The problem of getting a reliable, accurate analyzer that will operate satisfactorily with short pulses has been surprisingly difficult. A single channel design by Francis, Bell & Gundlach (42) is known to produce good results; recent modifications are as yet unpublished. When very low counting rates are encountered a multi-channel analyzer will save a great deal of time. On the other hand, these instruments are large and fairly expensive.

The equipment described above, plus a scaler, is all that is required for measuring β-ray spectra. While the resolution is considerably poorer than

that obtained with a magnetic spectrometer, it can be used with much weaker sources since 50 per cent of the β-ray are counted and the source may have considerable area. With such an instrument Bell & Cassidy (33) were able to demonstrate that the spectrum of Be^{10} has an unallowed shape. The instrument was also used to measure the K^{40} spectrum (34).

With the source mounted just outside the crystal, the observed β-ray spectrum always departs from the straight line Fermi-Kurie plot at low energies due to the fact that some of the higher energy β-rays are scattered out of the phosphor before coming to rest. By splitting the phosphor in half and mounting the source between the halves, Ketelle obtained a straight line plot down to 30 k.e.v. electron energy (62). The split crystal has 100 per cent geometry. This is advantageous in determining the number of disintegrations but presents a problem under some circumstances. For example, if a certain isotope decays by emitting a β-ray and a highly converted γ-ray, then one

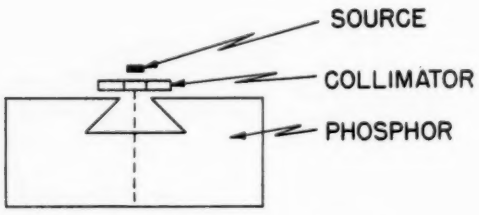

FIG. 2. Hollow crystal detector.

will observe not the β energy, but the sum of the β and conversion electron energies. Even when the γ-ray is not highly converted, enough of the γ-rays may be absorbed in the crystal to change the shape of the β-spectrum and make endpoint determinations unreliable. As a consequence, Bell is now using another technique. The phosphor has a conical hole drilled in it as shown in Figure 2. The β-rays from a source are collimated so that they strike only the bottom of the hole and have, therefore, a small probability of being scattered back out of the hole. The β-spectrum of Ca^{45} has been measured with this spectrometer; a Kurie plot of the data is shown in Figure 3. Note that the points fall quite closely on a straight line down to 50 k.e.v.; below this energy the points lie below the line rather than above as is usually observed in scintillation spectrometers. Correction for the nonlinearity of pulse height versus energy for anthracene has been applied.

γ-Ray energy measurements.—Although the early work of Kallman and others showed that scintillation counters could be used to measure γ-ray energies, the technique has come fully into use only during the past year. The improvements in tubes and techniques and the discovery by Hofstadter of the scintillation properties of NaI(Tl) are largely responsible for the increased interest in this field. Johansson (55) early showed the usefulness of the method; the technique has been improved and exploited by

Hofstadter & McIntyre (51, 66), Bell & Cassidy (34, 36), and Pringle & Standil (70, 71).

The β-ray spectrometer described in the last section can be readily adapted for γ-ray measurements. The anthracene should be replaced by a NaI(Tl) crystal in the form of a cylinder about $1\frac{1}{2}$ in. diameter and length. Since NaI is very hygroscopic, it is necessary to keep the atmosphere away from it. Bell mounts his crystals inside a polished aluminum cup which is hermetically sealed by a lucite plug in the open end. The lucite plug serves as a "light piper" for connecting the crystal to the photomultipliers. (See Fig. 4.) The

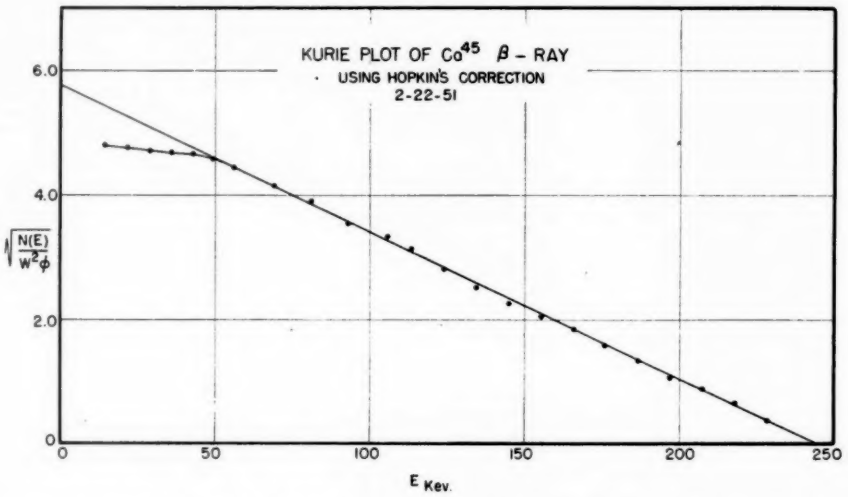

FIG. 3. Kurie plot of Ca^{45} β-ray using hollow crystal spectrometer. The observed data has been corrected for nonlinearity of pulse height versus particle energy.

differentiation time constant of the amplifier may need to be lengthened—somewhere between $\frac{1}{2}$ and 1μ sec. is suitable for this particular phosphor. Too short a time constant will give spurious pulses; too long reduces the maximum counting rate unnecessarily. Either an R-C or delay line differentiating circuit can be used; the analyzer problem is a bit easier with delay line differentiation.

When the crystal is illuminated by monochromatic γ-rays, the resulting spectrum of recoil electrons can be used to determine the energy of the γ-rays. The reader is referred to the papers previously cited (36, 51, 70) for a complete discussion. γ-Rays are absorbed inside the crystal by photoelectric effect, Compton effect, and pair production. Figure 5 is the result of a calculation by Hughes (12a) on the magnitude of each effect in a NaI crystal as a function of γ-ray energy; the calculation did not take multiple scattering into account.

For low energy γ-rays the photoelectric effect is predominant and produces a single peak in the pulse-height distribution curve as measured by a single channel analyzer. Although one might expect two peaks due to conversion in the K and L shells, only one is observed and this at the full γ-ray energy. This is because the resulting x-rays are largely converted inside the phosphor and so add their energy to that of the photoelectron. (See page 222 also.)

When the γ-ray energy is between 0.3 and 2 M.e.v., the Compton process

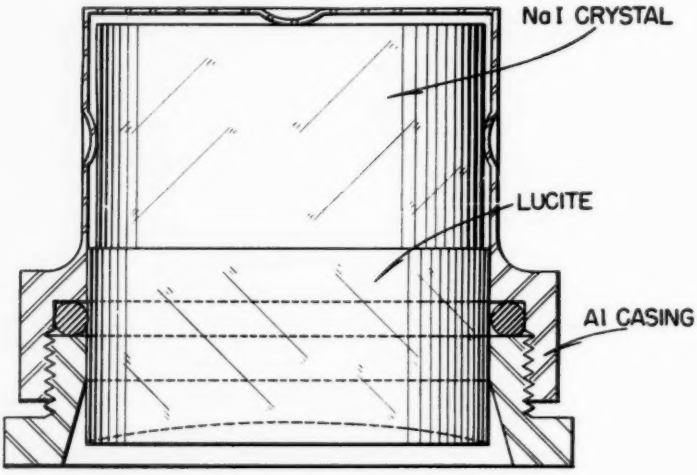

FIG. 4. A convenient mounting for NaI crystals.

becomes predominant. A monochromatic γ-ray of energy $h\nu_0$ produces recoil electrons of all energies up to a greatest energy, E_{max}, given by the equation

$$E_{max} = \frac{E_\gamma}{1 + \frac{mc^2}{2E_\gamma}}$$

where $mc^2 = 0.51$ M.e.v. The distribution in energy of the recoil electrons is fairly uniform, rising somewhat near the endpoint and then breaking sharply to zero. Figure 6, taken from Bell (1a), is the pulse distribution obtained from a NaI(Tl) crystal irradiated with 0.75 M.e.v. γ-rays from Cb^{95}. The Compton distribution can be seen as well as the photo-peak at higher energy. This peak is higher than would be expected from the photoelectric cross section. Actually, a good many of the Compton scattered γ-rays are absorbed inside the crystal so that all of the energy of the incoming photon is converted to electron energy. The hump in the curve at lower energies (below 400 divisions) is due to back scattered radiation. The source was mounted close to the crystal; hence, γ-rays that leave the source in any direction can return

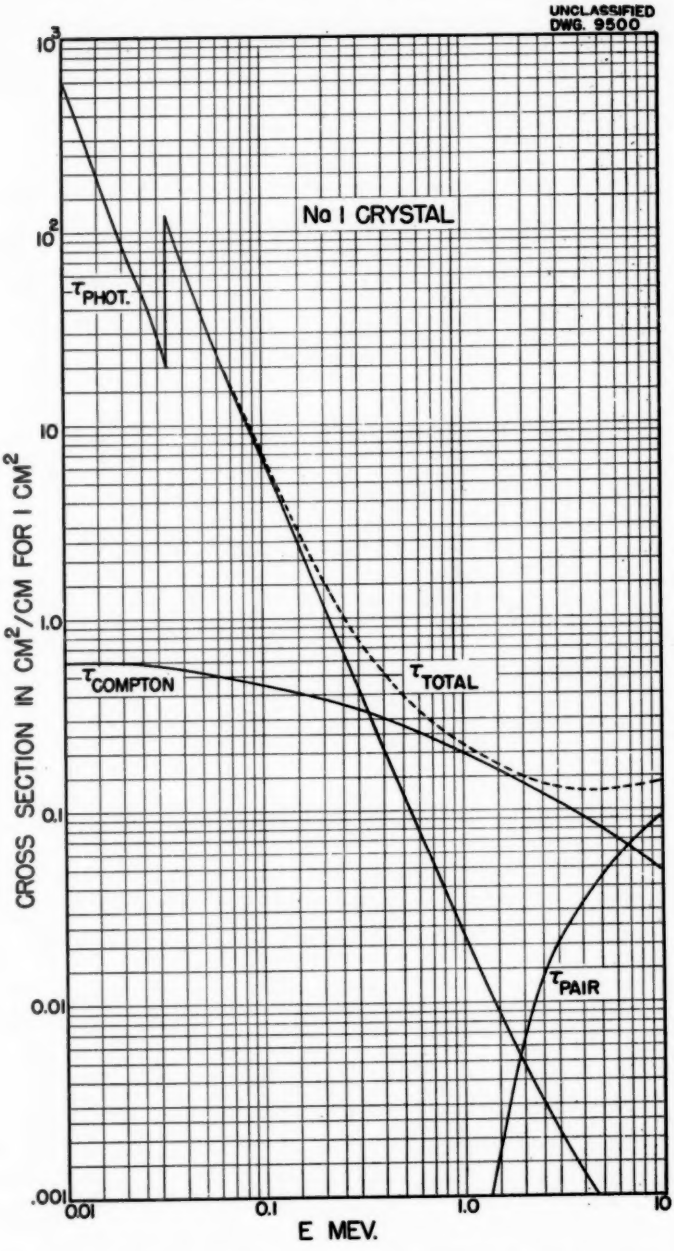

FIG. 5. The cross-section of NaI as a function of γ-ray energy.

to the crystal by 180° scattering in the walls surrounding the crystal and source. In this case, 180° scattered radiation has an energy of 190 k.e.v. (314 pulse-height divisions); doubly scattered radiation is of predominantly lower energy.

At γ-ray energies above 1.5 M.e.v. one observes not only the Compton

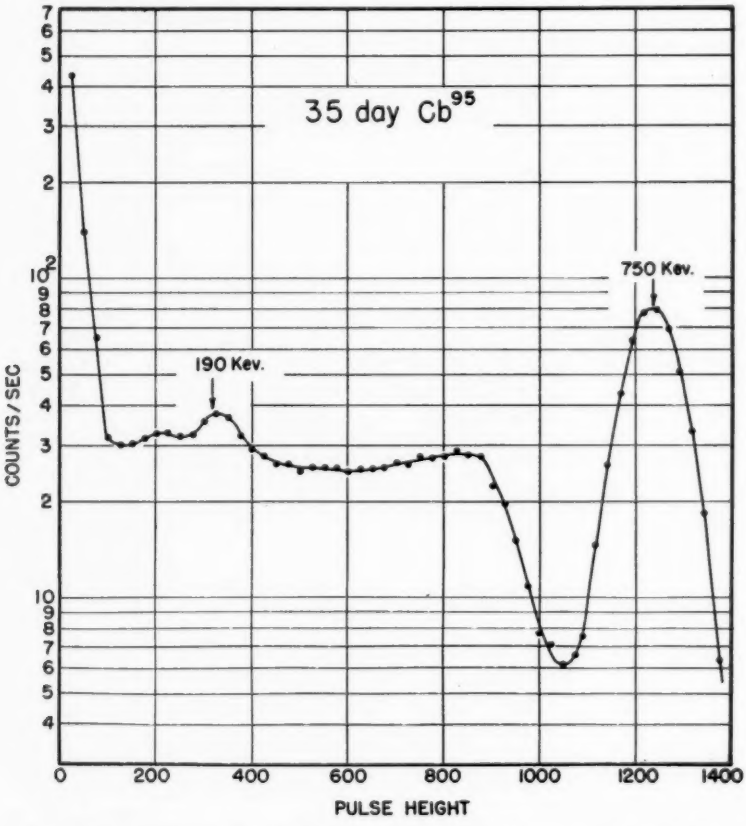

FIG. 6. The response of a NaI crystal to the 0.75 M.e.v. γ-rays from Cb^{95}.

distribution and an enhanced photo-peak, but also effects due to pair production. There will be a peak at the γ-ray energy minus 1 M.e.v. due to the positron-electron pair. When the positron stops in the crystal, two half-M.e.v. photons are created. One or both of these may be absorbed in the crystal. If both are absorbed, the photo-peak is further enhanced; the absorption of one photon results in a peak halfway between the pair and photo-peak. Figure 7 shows the pulse distribution produced by the γ-rays from Na^{24} on a NaI(Tl) crystal. The photoelectric peak and the pair peak due to the 2.76 M.e.v. γ-ray are well resolved. The peak due to pair formation with

the escape of one photon is superposed on the Compton distribution. The photo-peak from the 1.38 M.e.v. γ-ray and the accompanying Compton spectrum are readily seen.

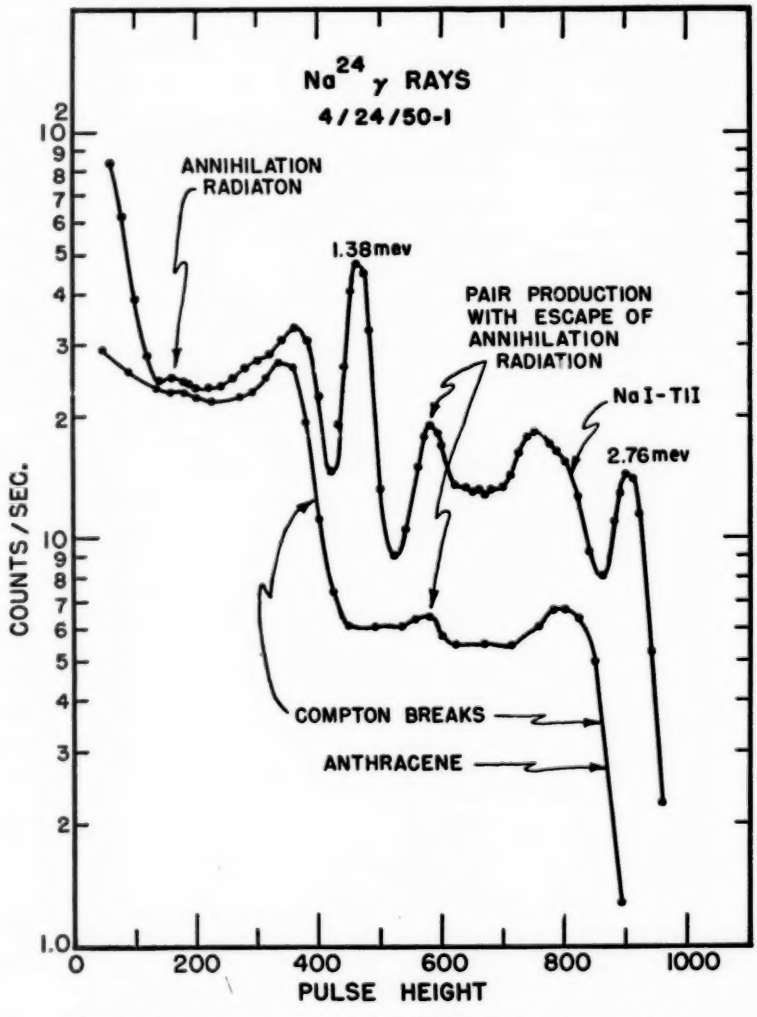

FIG. 7. A comparison of the pulse height distributions of NaI and anthracene to Na^{24} γ-rays.

When one attempts to analyze a complex γ-spectrum, he is embarrassed by the large number of fairly broad peaks due to each component. If the same spectrum is taken with anthracene in place of NaI, the pair and photo-peaks are almost completely removed, and one sees a series of steps at the

end-points of each Compton distribution. Although γ-ray energies cannot be determined as precisely with anthracene as with NaI, it is of considerable help in untangling the peaks of the latter.

It would, of course, be desirable for each γ-ray energy to give a single sharp peak in the pulse height spectrum. Several schemes for achieving this goal have been proposed and tested. A straightforward approach is to make the NaI(Tl) crystal so large that essentially all of the secondary photons from Compton scattering or positron annihilation are absorbed in the crystal. Crystals 4 in. in diameter and length are being tested by Bell at Oak Ridge. At the time of writing he has not been able to get as good resolution as with small crystals; this may be due to poorer material in the large crystal or poorer light collection. The latter difficulty should be alleviated when tubes with large photocathodes are available (1a).

A second approach to the problem has been proposed by Hofstadter & McIntyre (50). A beam of collimated γ-rays is directed onto a NaI(Tl) crystal as shown in Figure 8. γ-Rays which make Compton collisions in

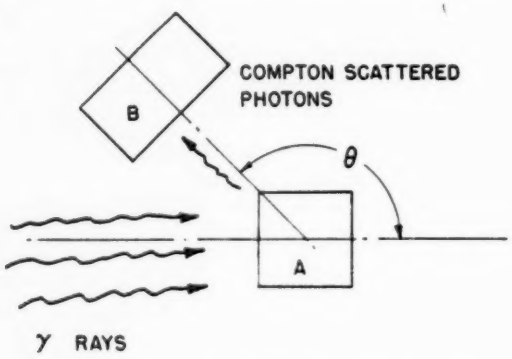

FIG. 8. Two crystal scintillation spectrometers.

crystal A give rise to scattered photons, some of which are detected in crystal B. A coincidence scheme is used to measure the height of the pulse in A when a simultaneous pulse is recorded in B. When θ is large ($>135°$), the γ-ray energy is simply related to the recoil electron energy and nearly independent of θ. Thus, by measuring only forward scattered electrons, one obtains a one to one correspondence between electron energy and γ-ray energy. Hofstadter's curves on Co^{60} show the 1.1 and 1.3 M.e.v. lines well resolved with relatively few counts at energies below the Compton peak. He does not extend the curve to low energies where one might expect counts due to forward scattered photons in crystal A being back scattered by surrounding materials into crystal B. With γ-rays of 2 M.e.v. or higher, two peaks appear due to pair production in A, B being triggered by annihilation radiation. This effect could probably be alleviated by using anthracene for the scattering

crystal and accepting only those pulses from B whose heights correspond to energies in the region of $1/2\ mc^2$.

The double crystal method outlined above requires much stronger sources than the single crystal detector. First, only a small fraction of the photons passing through the scattering crystal produce counts. Second, the source must be located at some distance in order to get a beam of γ-rays that is collimated to within some 10°.

Another scheme of measuring high energy γ-rays has been proposed by Johansson (56) and independently by Bair & Maienschein (30). Three NaI crystals and associated multipliers are placed in a linear array. Pairs produced in the center crystal are measured when annihilation radiation (from the positron member of the pair) is detected simultaneously in the side crystals. Thus, a pair spectrometer of moderately good efficiency is obtained. Since the γ-ray beam need not be collimated, the instrument can be used in a surrounding flux or with the source adjacent to the crystal. Johansson has tested the instrument with Sb^{124}; the 1.7 and 2.1 M.e.v. peaks are well separated. Bair & Maienschein used the 2.62 M.e.v. γ-ray from a 1 μc. source of ThC″ and found the full width at half maximum to be less than 10 per cent. Approximately 0.25 per cent of the γ-rays through the crystal were counted. While this is considerably less than can be obtained with single crystals (20 to 40 per cent) it is high compared to the usual pair spectrometer. Source strengths of 1 μc. of ThC″ are sufficiently intense for the scintillation spectrometer; a magnetic pair spectrometer requires some 10 mc. (76).

Other applications of scintillation counters.—Scintillation counters have been widely used for determining the time relationships in nuclear events. Some phosphors emit light with a time constant less than 10^{-8} sec. There is no measurable delay between the passage of the particle and the time for the emitted light to reach maximum intensity.[2] There is a transit time in the photomultiplier of some 10^{-8} sec. which is ordinarily of no concern to the user; on the other hand, the spread in transit times is some 10^{-9} sec. and may impose a limitation on time resolution (67). Several investigators are now using scintillation counters to measure the lifetimes and the spectra of short-lived nuclear isomers. Already one has been found with a mean life of 8×10^{-10} sec. and considerably shorter lives could be detected with present-day equipment.

The usefulness of coincidence scintillation spectrometers for determining nuclear decay schemes has been amply demonstrated. Two crystals are used, one on either side of the source. Each crystal has its own photomultiplier, amplifier, and pulse height analyzer. The output terminals of each analyzer

[2] More explicitly, one should say that the average rate at which photons are emitted is greatest immediately following the ionizing event. In practice, a number of photoelectrons must be released from the photomultiplier cathode before the coincidence circuit is triggered. The fluctuations in time of triggering have been considered by Post & Schiff (69).

are connected to a coincidence circuit. In a typical case, one might interpose a β-ray absorber between one crystal and the source and set the analyzer associated with that crystal on the photo-peak of a given γ-ray. The other analyzer could then be used to measure the spectrum of the β-rays in coincidence with the γ-ray. An absorber between the source and the second crystal will permit one to measure the recoil electron spectrum of the γ-rays in coincidence with the given γ-ray. The application of the coincidence technique will justify considerable confidence in the energy level assignments and enable one to detect weak β-rays that would almost certainly be missed by the usual techniques.

A γ-ray scintillation spectrometer, in conjunction with a magnetic lens spectrometer, has proven very valuable in determining decay schemes and beta-gamma angular correlations (39a). The technique is very similar to that described previously for two scintillation spectrometers.

Scintillation counters for α-particle detection are in use in many laboratories; they have some minor advantages over thin-window and air proportional counters, but no overwhelming superiority.

Portable scintillation counters for detecting low intensity γ-rays are considerably better than the usual Geiger counter sets. The high detection efficiency of a large sodium-iodide crystal produces moderately high counting rates so that a small increase in intensity can be detected in a relatively short time. In addition the cosmic ray background becomes relatively smaller because the sensitive volume is still about the same as that of a Geiger counter. Portable scintillation counters have been used for surveying areas for radioactive contamination; they have been flown in airplanes for uranium prospecting.

Scintillation counters have recently been used to replace the Geiger counter in conventional β-ray spectrometers. Baffles are always built into such spectrometers to reduce the background of off-energy electrons reaching the detector but are never 100 per cent effective. If the electrons are detected with a scintillation spectrometer, the bias of the single channel analyzer can be set to detect only those electrons which satisfy the field requirements of the β-ray spectrometer. The background is thereby reduced, not only by eliminating the counts due to scattered electrons but also the counts due to cosmic ray particles or other interfering sources. The latter is of particular importance when one is dealing with relatively weak β-ray sources; the background can be reduced by a factor of 50 or more.

Proportional Counters

Proportional counters have been used for many years to detect alpha particles and other energetic heavy particles. They have obvious advantages over an ionization chamber; the pulses are large so that the associated amplifier can be simplified; more capacity can be tolerated in the cable between chamber and amplifier; interference and amplifier noise are much less troublesome. The rise time of the pulse can be made quite short, being chiefly

limited by the difference in the time of arrival at the central wire for ions at the extreme ends of the ionizing track. There may, however, be a net delay from the time of the initiating event. With sufficient care, the pulse height can be made proportional to the number of ions generated by the primary particle, independent of the location of the track [Rossi & Staub (17)].

To achieve the advantages just mentioned, one must be willing to pay close attention to several details. First, a nonattaching gas must be used. The central wire must be highly uniform in diameter with no sharp points or dust particles. Insulators must be kept well away from the multiplying region so that any charges accumulated on them will not distort the collecting fields. An accurately regulated high-voltage supply must be provided. Care must be taken to insure that the insulators do not introduce spurious pulses when the high voltage is applied. At very high counting rates, the multiplication is reduced by the positive ion cloud.

End effects.—Unless considerable care is taken in designing a counter, the electric field will be distorted near the ends of the cathode wire. This results in a poorly defined sensitive volume and a marked dependence of pulse height on the position of the ionizing particle. Several schemes for reducing end effects have been used [see Rossi & Staub (17)]. Of the approximate solutions, perhaps the best is to support the cathode wire at the ends with larger wires. If the diameter of the end wire is made no larger than is necessary to reduce the multiplication to one, then the distortion of the field is fairly small over most of the sensitive region. More elaborate precautions are required if the field is to be kept accurately radial. One possibility is semiconducting disks near each end of the counter, but this has not worked out too well in practice. Another is to use coaxial end supports the same size as the anode wire, the signal lead being the center wire of the coaxial wire. This solution necessarily limits the minimum size of the wire, so that very high potentials are required to get appreciable multiplication. A more practical, and apparently quite successful, scheme has been tested by Cockroft & Curran (86). This involves the use of coaxial field tubes surrounding the ends of the wire. The potential of these tubes is chosen to make the electric field radial; the result is a counter having uniform sensitivity throughout a well-defined region.

β-Proportional counters.—The foregoing considerations have been analyzed in detail by several writers and will not be repeated here. On the other hand, one of the most interesting and important of the recent developments has been the use of proportional counters for the measurement of low energy β-particles and γ- or x-ray photons (81, 83, 88, 105). When a mixture of argon and methane is used for filling the counter, high gas multiplications can be used and yet remain in the proportional region. Thus a 600 e.v. β-particle produces some 20 ion pairs; by using a gas multiplication of 1,000, a charge of 20,000 electrons is collected. With reasonably low capacitance a voltage pulse is produced that is well above the noise threshold of a good linear amplifier, so that the voltage pulse can be measured accurately. Multiplications up to

10^6 can be used on single electrons (87). It appears that the multiplied charge should not exceed about 3×10^6 electrons for good proportionality.

One would not expect good energy resolution for low energy β-particles. The number of ion pairs formed is small and should be subject to some fluctuation. Also the gas multiplication should introduce a further spread. Curran *et al.* (87) have investigated both of these effects and find that they are of about equal importance in producing fluctuations. It is interesting to note that the spread in pulse height is less than simple statistics would indicate. Monoenergetic β-particles that produce $\overline{N}$ ion pairs on the average have a deviation less than the square-root of $\overline{N}$ (93); even after considerable gas amplification the deviation is only slightly larger than $(\overline{N})^{1/2}$. For example, the measured deviation in pulse height produced by an 8 k.e.v. electron is only 5 per cent and becomes considerably better for higher energies.

The usefulness of the β-proportional counter in nuclear physics has been amply demonstrated; Curran *et al.* (90) have measured the β-spectrum of tritium and found an allowed shape with an endpoint of 17.9 k.e.v. X-ray emission lines can be measured fairly accurately and with good efficiency; since the x-rays are absorbed in the counter chiefly by photoelectric effect, one will observe a prominent peak in the pulse height distribution corresponding to the energy of the x-ray photons. Lower energy "escape" peaks may also be observed when, for example, a xenon filled counter is used to detect x-rays having an energy greater than the K-binding energy of a xenon atom. K_α and K_β x-radiation will be excited, and some of these photons may leave the counter without being absorbed in the gas. In that event, the pulses produced will be correspondingly smaller than those resulting from complete absorption of the incoming photons. These escape peaks are commonly seen with proportional counters and have also been observed with scintillation counters (77).

Since β-proportional counters are used with a high value of gas amplification, considerable care must be exercised in choosing the filling gas. Not only must the gas have a low attachment coefficient for electrons, but it must also be a "quenching" gas which requires the addition of some polyatomic constituent. Argon plus 10 per cent methane is commonly used. If it is desirable to detect low voltage x-rays with good efficiency, then xenon or krypton may be used with methane. In counting low energy electrons from a source inside the counter, pure methane can be used, thereby reducing the sensitivity to any interfering x-radiation. Pure methane has the disadvantage of requiring higher voltage and may not give a pulse whose height is strictly proportional to the energy of the particle (89).

Proportional counters have been largely used to supplement scintillation counters in the low energy region. Proportional counters have the decided advantage of producing one electron for each 30 e.v. of particle energy; a scintillation counter produces one photoelectron for approximately 1,000 e.v. of particle energy. Thus, proportional counters can detect lower energy

particles or measure particles of a given energy with considerably less spread.

The upper energy limit of β-proportional counters has been limited to some 100 to 200 k.e.v. by the necessity of keeping the dimensions of the counter large compared to the range of the electrons. This upper limit promises to be extended up to 2 M.e.v. by the addition of an axial magnetic field (91, 107), which curls the electron trajectories to keep them inside the sensitive volume.

In addition to their many applications in the field of energy measurement, β-proportional counters have proven very useful for straight counting operations. Geiger counters suffer from the disadvantage of having a long recovery time after the passage of a particle. In addition the commonly used self-quenching counters have a limited life—in many counters the plateau is noticeably poorer after some 10^7 counts. This limits their usefulness where high counting rates are involved. β-Proportional counters are not subject to these limitations. They do not have a recovery time in the usual sense; the pulse rise time is very fast hence the counting rate is usually determined by the associated circuitry. When used with a high gain amplifier, the required number of ion pairs formed per pulse is relatively small, so that even when a quenching gas such as methane is used, the life is practically infinite. If the associated amplifier has good overload characteristics, one obtains a long and very flat plateau. Their only disadvantage, compared to a Geiger counter, is the need for a fairly high gain amplifier.

For high speed coincidence work, both Geiger and proportional counters are limited by the delay introduced between the passage of the particle and the collection of the electrons at the central wire. This has been measured by several investigators and is of the order of 10^{-7} sec. for a very small counter and several microseconds for a large counter.

Ionization Chambers

Pulse type ionization chambers still play an important role in the detection of nulcear particles. Although only the most elementary principles are involved, the mechanism is so frequently misunderstood that a brief review of the important features will be presented.

Consider first two parallel plates spaced a distance d apart, the upper plate being maintained at a positive potential V, as shown in Figure 9. The lower plate is shown connected to ground through a resistance R which will be assumed to be (and usually is in practice) quite large, perhaps 10^8 ohms. If an ion pair is created in the gas between the electrodes, the positive ion will be slowly impelled to the lower plate; the negative ion (electron) will move very rapidly to the upper plate so long as it does not become attached to a neutral atom of the gas. The voltage waveform on the lower plate produced by the motion of the ions is shown in Figure 10. The rapid motion of the electron produces a sharp rise in voltage, followed by a very much slower rise due to the positive ion. The total voltage rise is given by $V_2 = e/C$, C

being the total capacity of the lower electrode measured with respect to everything around it. The amount V_1, due to the electron collection is, in this case, $(x/d)\ V_2$. More generally, the height of the pulse due to the electron motion is the ratio of the potential that it falls through to the total potential across the chamber. The time t, required to collect the electron, is of the order of 1μ sec. Hundreds of microseconds may be required for the positive ion to cross the chamber.

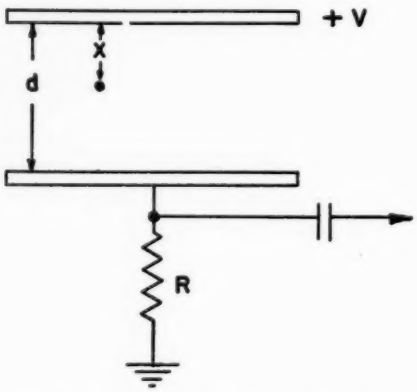

FIG. 9. Parallel plate ionization chamber.

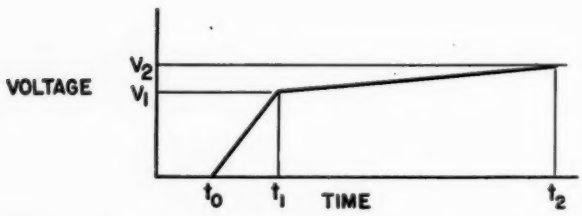

FIG. 10. Voltage waveform from a parallel plate chamber. The rise between t_0 and t_1 is due to electron collection; positive ion collection produces the rise between t_1 and t_2.

When an α-particle or energetic proton traverses the chamber, thousands of ion pairs are created, and the voltage pulse is large enough to be detected at the output terminals of a high gain amplifier whose input terminal is connected to the chamber. It is modern practice to use an amplifier with good enough high frequency characteristics to respond to the steeply rising electron pulse; the low frequency cut-off is purposely made fairly high so that the slow voltage rise due to the positive ions is discarded. This has important advantages: (*a*) the pulses out of the amplifier are short, thereby permitting high counting rate and negligible "pile-up"; (*b*) troubles with microphonics

and hum are greatly reduced. On the other hand, the disadvantages are apparent. First, the height of the pulse from a single electron depends on where in the chamber it is produced. Second, the gas in the chamber must be chosen with care because of electron attachment.

Energy measurements.—It is often desirable to use ionization chambers to measure the energy of the primary particle. For energy measurements, the voltage pulse from each electron should be the same height, then the total voltage pulse will be proportional to the number of ion pairs generated by the primary particle. Several schemes for avoiding the dependence of pulse height

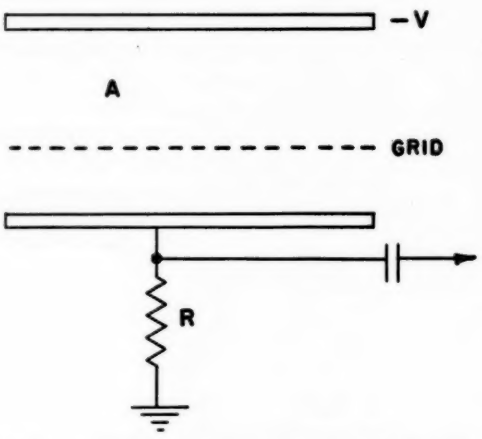

FIG. 11. Parallel plate chamber with Frisch grid.

on the location of the ionizing event are in use. In some cases, the ionizing particles can be collimated so that their tracks in the chamber are all oriented similarly and start at the same distance from the collecting plate.[3] For example, an α-source could be mounted on the collecting electrode and then covered with a flat metal plate having a number of fine holes drilled perpendicularly through it. The source and collimator could equally well be mounted on the high voltage electrode. In that case, a negative high voltage should be used to force the electrons to traverse as large a fraction of the applied potential as possible.

In the majority of experiments, collimation of the particles is impractical, but it may still be possible to confine the ionizing events inside a given region of the chamber. Under such circumstances, the use of a "Frisch grid" may be indicated. Figure 11 shows such a gridded chamber, the tracks of the primary particles being inside region A. The potential of the grid is chosen

[3] The collecting electrode is defined as the electrode to be connected to the amplifier grid.

slightly more negative than the potential of this surface with the grid absent in order to avoid appreciable collection of electrons by the grid. As the electrons move from their origin to the surface defined by the grid, very little charge is induced on the collecting electrode; the motion of the electrons between the grid and the collector produces a voltage change at the collector of e/C, C being the total capacity of the collector with the grid in place. Thus, all electrons originating above the grid produce the same size pulse. The proper spacing and size of the grid wires must be chosen rather carefully. The design of such chambers has been investigated by Bunemann *et al.* (84), who have succeeded in obtaining a resolution of approximately 50 k.e.v. with 5 M.e.v. α-particles.

Another method for reducing the dependence of pulse height on the origin of the ions is to use a fine wire or a small sphere for the collector (109). Since most of the voltage drop occurs in a small region surrounding the wire, and nearly all of the ionization is outside this region, each electron produces nearly the same size pulse. This method is simpler than the gridded chamber, works quite well even when the ionizing particles occur throughout the chamber, and results in a small collecting electrode capacity. The major disadvantage is the small collecting field over most of the chamber, an important item when the pressure or constitution of the gas is such that electron attachment is appreciable. A single wire chamber with 5 mil wire has yielded a resolution of 100 k.e.v. (full width at half maximum) with 5 M.e.v. alpha particles.

The methods described in the last two paragraphs for improving the energy resolution of the chambers have the disadvantage of introducing a delay between the ionizing event and the beginning of the pulse. The delay is due to the fact that the ions (electrons) must travel to a point close to the collecting electrode before an appreciable voltage rise can be observed. With the parallel plate chamber, the voltage starts to rise the instant the ionization occurs. This may be an item of considerable importance in coincidence experiments. If a parallel plate chamber is connected to an amplifier with a rise time and a fall time (determined by the differentiating network) that are short compared to the collection time of the electrons in the chamber, then the pulse waveform at the output terminals of the amplifier is a measure of the current in the chamber during the collecting interval. The length of the pulse is determined by the collection time; the height of the pulse, by the number of electrons generated by the primary particle, independent of the origin of the track. This method was developed by Sherr & Peterson (126) and works well with energetic particles where signal to noise ratio can be sacrificed.

Filling gases.—Considerable attention must be paid to the nature of the gas in the chamber; the electrons must arrive at the collecting electrode without becoming attached to neutral gas molecules. Only a very small amount of oxygen or water vapor will soak up the electrons completely.

Traces of some organic vapors will prevent electron collection; thus some types of insulators must be avoided because of their vapor pressure. We have found, for example, that some teflon insulators gave trouble; other investigators have used teflon without ill effect. Such problems are more serious in a sealed chamber than in a chamber through which gas is circulating. With argon filling, the Los Alamos group frequently use a hot calcium metal purifier attached to their ionization chambers; the argon is continuously recirculated through the calcium to keep the gas free of impurities. On the other hand, we have achieved quite satisfactory results by connecting a tank of commercial argon to the chamber and letting it flow through the chamber at the rate of 1 or 2 cu. ft. per hr.

For some applications, it is desirable to use gas at high pressure in the chamber; the demands on impurities are correspondingly more stringent. Wilson, Collie *et al.* (85, 109) have succeeded in purifying hydrogen, deuterium, and methane to obtain electron collection in chambers operating at 35 atm. The oxygen concentration was reduced to less than 1 p.p.m. High pressure operation with argon or helium is not particularly troublesome because the purification of noble gases can be readily accomplished.

BF_3 is frequently used as a filling for ionization chambers and proportional counters for neutron detection. Fowler & Tunnicliffe (95) have recently developed a method of purifying this gas and find that a freshly filled counter gives excellent results; in fact the two α-groups from the $B^{10}(n, \alpha)Li^7$ reaction are readily resolved. Within a few days, the counter deteriorates and the pulses become smaller and the resolution poorer, probably due to impurities released as the BF_3 reacts with the walls of the chamber. If the counter is aged for some weeks and then refilled with pure BF_3, a stable counter results. Bistline (82) has shown that even with purified BF_3 the attachment coefficient is such that high collection voltages must be used if the electrons must travel a few centimeters. For example, with an E/p (where E is the electric field strength and p the gas pressure) of 10 v./cm./cm. of Hg, the "average" drift distance before capture is only 3 cm.

Ionization chambers have been operated with other than gaseous filling. Liquid argon has been used but the required field is inconveniently high. Crystal media have been limited in their usefulness, partly by the high field strength required but chiefly by the polarization effects.

Drift velocity.—The time required for the electrons to reach the collecting electrode depends upon the drift velocity of the electrons as well as the distance traversed. Rossi & Staub (17) have described the extensive investigations carried on at Los Alamos on the drift velocity, W in various gases as a function of E/p where E is the electric field strength and p the gas pressure. Drift velocities between 10^6 and 10^7 cm. per sec. are commonly encountered. Unfortunately, electrons in pure argon have a very low drift velocity. We have made measurements with spectroscopically pure argon circulated over hot calcium metal and oxidized copper and found the drift velocity to be

only 3×10^5 cm. per sec. at an E/p of 0.4 v./cm. mm. Hg. The addition of a small percentage of CO_2 will increase the velocity by a factor of five and is commonly used in ionization chambers. The higher drift velocity and lower electron energy is of advantage in decreasing the pulse length and in reducing the effect of small impurities which might capture electrons (24). Bistline's results on the drift velocity in BF_3 are considerably lower than reported by Rossi & Staub, the former observing a velocity of approximately 10^6 cm. per sec. when E/p is 10 v./cm./cm. of Hg. Recent unpublished work by Pawlicki (15a) confirms Bistline's data.

Since ionization chambers are frequently used for measuring particle energies, it is important to know the relation between the number of ion pairs produced in the gas and the energy lost by the particle in the gas. The ionization produced by α-particles was investigated by Gurney (99) and Gray (98) and more recently by Jesse, Forstat & Sadauskis (102). It appears that in noble gases such as helium, neon, and argon, a strictly linear relationship exists. In air, on the other hand, the amount of energy required to produce an ion pair is not constant but becomes significantly larger for low energy α-particles.

γ-Ray spectroscopy.—The possibility of using ionization chambers for high-energy γ-ray spectroscopy has long been considered. If a chamber is filled with deuterium (or deuterated methane) and irradiated with γ-rays, photo-protons will be produced having an energy of half the difference between the photon energy and the deuterium binding energy.[4] Early attempts at measuring γ-ray energies by this method were unsuccessful because the amplifiers were relatively slow (positive ion collection) and hence the "pile-up" due to Compton recoils obscured the photo-protons. Recent improvements in the deuterium purification technique (109) have made electron collection possible and consequently much shorter resolving times. The technique is being exploited by Wilson, Collie & Halban (111) and promises to compete favorably with a pair spectrometer. Wilson (25) has used it to measure neutron capture γ-rays and obtained moderately good resolution. The estimated resolution at 8.5 M.e.v. is approximately 10 per cent; at lower energies, it becomes considerably better, perhaps 4 per cent at 3.5 M.e.v. Deuterium loaded photographic plates have also been tried for γ-ray measurement (123); the chief disadvantage is the tediousness of measuring large numbers of proton tracks.

Neutron Detection

Neutron measurements can be divided into three principal categories: (*a*) slow or thermal neutron detection, (*b*) fast neutron detection, (*c*) measurement of neutron energies. The divisions are listed in order of their diffi-

[4] The momentum of the incoming photon produces some uncertainty in the energy of the recoil proton. Conversely, the "calculated" energy of a photon may be in error by some 10 per cent in the region of 10 M.e.v.

culty; only the first can be said to be well in hand. One of the major obstacles to overcome is the inability of most detectors to discriminate against γ-rays since neutrons are almost invariably accompanied by γ-rays.

Slow neutron detection.—Slow neutrons can be readily detected with good efficiency by any of a variety of methods. One of the simplest and most accurate methods is to expose a thin foil of some material having a high activation cross section for the neutrons and then measure the (n, γ)-induced β-activity with a thin window counter or γ-activity with a scintillation counter. One of the advantages of the foil method is its complete insensitivity to γ-radiation of energy less than 6 M.e.v. Indium foils can be readily used to measure thermal neutron fluxes down in the region of 1 neutron/cm.^{2}/sec. Presumably the lower limit would be that imposed by the natural activity of In^{115}.

When continuous monitoring of neutron flux is required, the foil method is obviously unsatisfactory. In such instances, a measurement of the current in a boron-coated or a BF_3-filled ionization chamber is frequently used. The neutron flux level must be fairly high to obtain a readily measurable current and the gamma background must be relatively low if the γ contribution to the current is to be kept small. The effect of the γ-rays can be greatly reduced by using a compensating chamber without boron, the γ-current from the compensating chamber bucking-out the γ component from the boron lined chamber.

At lower flux levels, it is advantageous to use BF_3-filled or boron coated chambers as pulse chambers; the bias on the pulse height selector following the amplifier can be set to discriminate against a fairly intense γ-ray background. The large cross section for the B^{10} $(n, \alpha)Li^7$ reaction (3,800 barns) and the recent availability of separated B^{10} has permitted high detection efficiency. Usually such chambers are operated as proportional counters because it is more convenient to deal with large pulses. Proportional counters, approximately 50 cm. long and filled with enriched BF_3 to a pressure of 40 cm. Hg have been built with a detection efficiency of 80 per cent for thermal neutrons traveling along the axis of the counter.

The difficulty in purifying and maintaining the purity of BF_3 has led many investigators to prefer boron-lined chambers. The boron can be applied by mixing the powdered boron with a thin lacquer and painting the surfaces to be coated with a brush dipped in the solution. More adherent coatings can be obtained by painting the surfaces with a colloidal suspension of boron in oil and then heating the surface to red heat in an induction furnace through which nitrogen plus 10 per cent hydrogen is flowing. Another process is to deposit elemental boron from diborane at high temperatures. This method requires fairly elaborate equipment and involves some explosion hazard. For maximum detection efficiency with a boron coated chamber, multiple plates should be used. The question of optimum coating thickness has been discussed by Lowde (122). It is obvious that there is no point in

making the coating thicker than the range of the α-particle; actually the loss in efficiency of a single plate is small when the thickness is reduced to half the α-particle range. In a multiplate chamber, it is advantageous to use still thinner coatings in order to reduce the absorption of neutrons in B^{10} nuclei which do not give detectable alphas. Lowde describes a 12-surface chamber, slightly over 2 in. long, that has a detection efficiency of 24 per cent.

When the γ-ray background becomes too intense, the pile-up of pulses due to recoil electrons in the chamber will exceed those due to α-particles. Under such circumstances the use of fission chambers is indicated (17). The large pulse obtained from the fission fragment will override almost any γ-ray flux, especially when used with fast amplifiers. The sensitivity compares favorably with the foil method when U^{235} is used for coating the plates.

Fast neutron detection.—Fast neutrons can be detected by any of several techniques, such as hydrogen or methane filled proportional counters, photographic emulsions, foil excitation, fission chambers, and scintillation counters. All have proven very useful, none ideal under all circumstances. There is as yet no fast neutron detector that has (*a*) high efficiency, (*b*) γ-insensitivity, and (*c*) prompt response to the passage of a fast neutron. The ideal detector would have these three properties plus the added one of producing a voltage pulse proportional to the neutron energy.

The problem of obtaining high efficiency is chiefly due to the small scattering and absorption cross sections at high neutron energies. One way of avoiding this dilemma is to interpose a moderator such as graphite or paraffin in the fast neutron beam. The neutrons are slowed down in the moderator and can then be efficiently detected in a boron chamber. One of the advantages of such a detector is that it can be made to have an efficiency that is almost independent of neutron energy. Such counters are fully described by Rossi & Staub (17); though in general use for monitoring low fluxes of fast neutrons, they are bulky and have a relatively slow response time. To avoid these difficulties, another scheme has been proposed, namely that of capturing the neutrons in a mass of cadmium or boron. The capture is announced by the emission of one or more γ-rays which can be detected efficiently in a large NaI crystal scintillation counter. Though possibly not as efficient as the foregoing scheme, the time lag is small and such detectors can even be used for coincidence experiments. The chief disadvantage is the sensitivity to stray γ-radiation. Actually, an anthracene scintillation counter is an efficient fast neutron detector, but can rarely be used since the crystal itself must be placed in the neutron beam where it counts the γ-rays which are also present with high efficiency. Frey (8) has painted a mixture of "poly-dope" (Amphenol "901" Cement) and zinc sulfide on the end of a 5819 photomultiplier tube; a flux of 1,200 neutrons per minute from a Ra-Be source produced 7.4 counts per minute due to recoil protons. The counter was quite insensitive to γ-rays.

Neutron energy measurements.—Photographic plates with emulsions 100

μ or more thick provide perhaps the most reliable method of measuring the energy spectrum of a collimated beam of neutrons. The most direct method is to expose the plate edge-on in the neutron beam. After developing, the plate is examined under a microscope; a measurement of the range and the angle of a recoil proton determines the energy of the scattered neutron. Corrections must be made for changes in the (n, p) scattering cross section, finite plate thickness, shrinkage after development, etc. Nevertheless, fairly good resolution can be obtained if one has the patience to measure a large enough number of tracks to get good statistics. Nereson & Reines (124) have given a detailed account of their work with neutrons of energy 0.2 to 1.5 M.e.v. The curves presented show good resolution, having a half-width of approximately 0.05 M.e.v. Others (116, 125) have used the technique for measuring nuclear energy levels.

A second method (114) is to place a photographic plate, in a vacuum, at some distance from a hydrogeneous radiator. Thus, the angle between the recoil proton and the neutron beam is already determined, and one has only to measure the range of the protons in the plate, making sure that the direction of the track is that determined by the geometry. Longer exposure times are required, but this time is usually negligible in comparison with the time for measuring the plate.

A third method makes use of Li^6 loaded plates, the neutron energy being determined by the range of the particles from the Li^6 $(n, \alpha)H^3$ reaction. This method has the distinct advantage of working with uncollimated neutrons. Unfortunately, the neutron energy is a double valued function of the sum of the ranges of the α-particle and triton. Keepin & Roberts (119, 120) have worked out a technique for developing the plates and choosing the tracks to be measured which enables them to measure neutron energies in the range 0 to 5 M.e.v. with a resolution of 0.1 M.e.v.

Determining neutron spectra by counting tracks in photographic plates is tedious and time consuming. Consequently, considerable effort has been devoted to devising a neutron detector that will do the job electronically. The results to date have not been entirely successful. The most direct approach is to measure the energy of the recoil protons in a hydrogen filled chamber or proportional counter. For a monokinetic neutron beam, the recoil proton energies will be distributed uniformly from zero up to the energy of the neutrons. Therefore, the first derivative of the pulse height distribution should give a peak at the neutron energy. Unfortunately, the actual situation is not so simple. Wall effects, positive ion effects, ionization straggling, etc., distort the ideal distribution. Moreover, one must record a large number of counts in order to get good statistics at all points of the distribution if neutrons of more than one energy are involved. It is preferable to discard the counts due to protons scattered at an angle to the beam for these serve only to mask the pulses due to forward recoils from lower energy neutrons. At the same time, it is necessary to reject pulses from γ-rays; this

is usually accomplished by keeping the chamber dimensions less than the range of moderately energetic electrons.

Giles (96) reports the use of a screen wall proportional counter 2 ft. long and 1 in. in diameter. In the space outside the screen is a set of proportional counters in anticoincidence with the inner wire. Thus, only those recoil protons that originate and remain inside the 1-in. cylinder are counted. This will include the short range, large angle protons in addition to the desired forward scattered protons; the ratio of the energies of these two groups is not as large as one would like, Giles reporting a factor of only three. Thus, a given counter might be used to study neutrons having energies between 0.5 and 1.0 M.e.v. A second counter, filled to twice the pressure, would then cover the region between 1 and 2 M.e.v., etc. The disadvantage of accepting large angle recoils is compensated by the increased efficiency; the proton radiator (gas filling) must be thick compared to the range of the recoil protons.

A modification of the above mentioned counter has been proposed but not yet tested. If one observes the current pulse from a proportional counter, the length of the pulse will depend upon the orientation of the proton recoil track. Recoils parallel to the central wire will produce a short pulse since all of the ions are collected simultaneously. Pulses from tracks oriented at an angle to the wire will be lengthened by the difference in collection time for electrons from the two ends of the track. By discarding long pulses, only tracks with a small component perpendicular to the wire will be counted and their voltage rise measured to give the energy of the incident neutrons. Wall effects would be more serious with this type of counter; on the other hand, large diameters could be used and more neutrons counted.

Another approach to the problem is to use a solid hydrogeneous radiator, collimate the recoil protons, and measure their range by coincidence proportional counters and absorbers (17, 24, 97, 112). By this means, the large angle recoil proton can be completely discarded. On the other hand, the efficiency is quite low since the radiator must be kept thin compared to the range of the recoil protons. For this reason, provision for changing the radiator thickness to correspond to the neutron energy is usually made. For example, a glycerol tristearate radiator 100 μg. per cm.^{2} thick will produce approximately 2 recoil protons for every 10^5 neutrons of energy 2 M.e.v. that pass through it (17). If now only those protons are counted that make an angle of 15° or less with the direction of the incident neutron, the efficiency is reduced to 1.5×10^{-6}. When one further considers that the neutrons from a given source must be collimated and that usually only a fraction of these neutrons are of the right energy to be counted, the source strengths required become very large if a reasonable counting rate is expected. A further difficulty that is frequently experienced with this type of counter comes from small amounts of hydrogeneous materials condensed on the walls of the chamber. Recoil protons from these walls (e.g., the proton absorber) may satisfy the conditions required for registering a count and yet have the wrong

energy. In spite of the difficulties, this method has been the most successful of any of the electronic counting techniques.

All of the methods of measuring the energy of fast neutrons so far described are unsatisfactory in one or more respects. Work is now in progress in many laboratories to improve the situation. He^3-filled proportional counters which make use of the (n, p)-reaction are being considered. Scintillation counters offer some intriguing possibilities. For example, if one could grow large clear crystals of LiI, a known scintillator, high efficiency detection of intermediate speed neutrons would be assured. In addition a measurement of the disintegration energy in the Li^6 (n, α) reaction would uniquely define the neutron energy. γ-ray background would still be a problem, though considerably alleviated by the circumstance that the Q of the reaction is high, namely 4.8 M.e.v. Growing good clear crystals of thallium-activated LiI has proven very difficult; however, Hofstadter *et al.* (52a) have recently succeeded in growing a crystal $4\times4\times6$ mm.^{3} The crystal was tinged with yellow and produced pulses one-tenth as large as NaI(Tl) when irradiated with γ-rays. Nevertheless, it produced good clean pulses when irradiated with slow neutrons.

Inasmuch as LiI is difficult to grow and is extremely hygroscopic, other lithium and boron phosphors are being investigated. Li_2SiO_3(Cu) and $Li_2Si_2O_5$(Ti) fluoresce when bombarded with α particles but with inconveniently long decay times (18).

Threshold detectors.—The difficulty of measuring the energy of neutrons has led to the use of resonance and threshold detectors to explore an unknown neutron spectrum. Cadmium covered indium foils are commonly used to detect the presence of epi-thermal neutrons (1.4 e.v. resonance absorption). Scattering resonances can be used at somewhat higher energies. Fission chambers using coatings of pure thorium or the separated isotope U^{238} are very useful for detecting the presence of neutrons above 1 M.e.v.

For neutron energies above 2 M.e.v., foil activation techniques again become quite useful. Phosphorus and sulfur, for example, become activated by the (n, p)-reaction, the resulting half lives being such as to be readily observed even in the presence of competing reactions. Unfortunately, the threshold ($\sim$ 1 M.e.v.) is not sharp, and one has to assume an "effective" threshold of some 3 M.e.v. (3). Between 9 and 20 M.e.v. the situation is somewhat better because many foils can be chosen which become unambiguously activated by the $(n, 2n)$-reaction. The thresholds are sharper than for the (n, p)-reaction. Silver is very good for neutrons above 9.6 M.e.v., carbon for neutrons above 20 M.e.v. The use of foils for threshold detectors has been recently investigated by Cohen (4) and the properties of the more useful ones listed (3).

Bismuth coated fission chambers are frequently used to detect neutrons above 50 M.e.v. It has also been demonstrated by Wouters that a photomultiplier (without phosphor) is sensitive to such very high energy neutrons.

He has suggested that the effect may be due to local heating of the photocathode by recoil nuclei.

Threshold detectors are useful for γ-rays as well as neutrons, the (γ, n)-threshold being the same as the $(n, 2n)$-threshold in center of mass co-ordinates. Foils exposed to energetic γ-rays become radioactive; the measurement of the activity is simpler for γ-rays since the competing (n, γ)- and (n, p)-reactions are absent. Instead of measuring the induced β-activity, one can detect the neutrons produced by the (γ, n)-reaction with boron proportional counters. Thus, materials can be used with thresholds from 1.68 M.e.v. (beryllium) to 18.6 M.e.v. (carbon). When deuterium is used (2.2 M.e.v.) a measurement of the energy of the photo-proton determines the energy of the γ-ray (see p. 234). Photofission reactions may be used with high energy γ-rays, the threshold being about 5 M.e.v. in uranium and thorium (14).

Acknowledgments.—The author gratefully acknowledges the help of Mr. J. E. Francis in the preparation of the bibliography. P. R. Bell, J. E. Francis, A. H. Snell, and E. O. Wollan have made valuable criticisms of the early manuscript.

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CHEMISTRY OF THE ACTINIDE ELEMENTS

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This review will concern itself primarily with the chemical literature appearing during the year 1950. Where the discussion requires it, publications before 1950 will be cited, but no systematic survey of all of the pertinent literature between 1945 and 1949 can be undertaken here.

The year has been an active one in this field. More than 200 publications dealing with various aspects of the actinide elements have appeared. The appearance of a number of volumes of the National Nuclear Energy Series has been particularly significant in bringing the results of much war-time research to the attention of the scientific world. Increasing attention has been devoted to some of the hitherto more obscure members of the actinide elements, especially elements actinium and protactinium. The greater portion of activity, however, remains concentrated on the chemistry of uranium and thorium, presumably because of their comparatively greater accessibility. Noteworthy during the period under discussion has been the discovery of elements 97 and 98, berkelium and californium. The electronic configuration of the actinide elements has generated a lively discussion which has done much to clarify the relationships of the actinide elements to each other and to the remainder of the elements in the periodic system.

General Reviews

Lister (81) has reviewed the chemistry of the transuranium elements, with emphasis on the comparative chemistry of uranium, neptunium, and plutonium. Haissinsky (59) has discussed the new synthetic elements and their relationship to the periodic system from the point of view of oxidation states and general chemical properties. Although not strictly speaking a systematic review, the National Nuclear Energy Series, Division IV, Volume 14B, entitled *The Transuranium Elements: Research Papers* (109), presents much of the war-time and postwar research of the Manhattan Project in the form of more than 150 research papers. These mainly deal with the chemistry and nuclear properties of plutonium, neptunium, americium, and curium, and provide a key to much of the earlier literature. A detailed summary of investigations in the field of uranium and thorium chemistry performed during the war at Iowa State College, Ames, Iowa, has been given by Nottorf (93). Hahn (57) has briefly surveyed the actinide elements, and Spence (114) has considered the chemistry of the actinide elements as it concerns the technological aspects of nuclear energy. The proceedings of a symposium on the chemistry of the heaviest elements held in Cambridge, England, in 1949 have been briefly summarized by Anderson (6), and Emeléus (38) has briefly reviewed the transuranium elements.

Electron Configuration of the Heaviest Elements

The earliest chemical studies on the transuranium elements made it clear that the heaviest elements form a transition series more or less similar to the rare-earth elements. That such a transition series should exist in this portion of the periodic table was probably first recognized by Bohr; Seaborg (107) has thoroughly reviewed the early literature. That the heaviest elements do in fact constitute a transition series of elements in which the 5f shell is successively being filled appears certain. Debate has centered, however, on whether the first member of the series is actinium, thorium, or uranium, and the exact electron configuration to be assigned to the various elements. Seaborg (106) has strongly advocated the view that the first element of this series is actinium, and that the series should properly be designated an actinide rather than a thoride or uranide series. The principal evidence adduced for this view lies in the marked similarity of gadolinium and curium, from which it is inferred that curium has a half-filled 5f shell just as does gadolinium. This would necessarily make actinium the precursor of the series. Seaborg (108) has made it clear that this view does not necessarily imply that the first 5f electron appears in thorium. On the contrary, it appears that in the early portion of the actinide series, the 6d orbitals are more stable than the 5f, and it is probably only in uranium that the first 5f electrons appear.

Haissinsky (60, 61) has been a leading advocate of the view that uranium should be considered the starting member of the new rare-earth-like series. His views are based almost entirely on chemical evidence and illustrate the difficulty of assigning electron configurations to ions exclusively on the basis of chemical data. Wylie (146) essentially agrees with Haissinsky & Paneth (96), in dividing the actinide elements into a cis- and transuranium group, primarily on the basis of chemical arguments. Conclusions of this sort, based purely on chemical behavior, have at the best dubious validity since the relationship between electronic configuration and chemical properties is not simple. In the case of the rare-earth elements, for example, Connick (23) has pointed out that the predominance of the +3 state and the great resemblance of the +3 ions to each other are to a certain extent fortuitous in that they result from the balancing of various factors such as ion radius and heats of hydration of the ions. An analogous electronic configuration for the actinide elements does not, therefore, imply the same degree of chemical resemblance that one finds in the lanthanide elements.

Glueckauf & McKay (51) have interpreted the behavior of uranyl salts in nonaqueous solvents on the basis of bond formation involving 5f orbitals of uranium. Katzin (70), however, disagrees with this view and points out that similar phenomena are observable with Co^{++} ions in nonaqueous solvents where no f orbitals can be involved. The full merits of these arguments still remain to be evaluated; the evidence in favor of 5f orbitals being involved in complex ion formation is still tenuous [see, however (118)].

The laboratory investigations directly concerned with the question of the electronic configuration of the heaviest elements have been regrettably

few in number. For the most part they have been either spectroscopic or magnetic studies. These are considered below.

Spectra.—Attention has been particularly directed to the emission spectra of thorium and curium during the period under review. Klinkenberg (73) has studied the spectrum of doubly ionized thorium. The Th(III) spectrum is revised to include 314 lines as transitions between 39 even and 40 odd levels arranged in two-term systems. The configurations 6d 7p and 5f 7p show pronounced *jj*-coupling. The ground state of Th(III) appears to be $6d^2\ {}^3F_2$; this level is 809.9 $cm.^{-1}$ below the $5f6d^3H_4$ state. The ionization potential of Th(III) is 19.9 v. Racah (101) finds these results of Klinkenberg to agree satisfactorily with theoretical calculations based on intermediate coupling with configuration interaction; the calculated g values also agree with the experimental data.

The spectrum of trebly ionized thorium has also been studied by Klinkenberg (74, 75). The ionization potential is approximately 28.6 v. It is shown by Zeeman effect studies that the ground term of the Th(IV) spectrum is $5f({}^2F_{5/2})$. Stukenbroeker & McNally (120) have observed isotope displacements in the spectra of Th^{230} and Th^{232}. The magnitude of the shift is approximately half that observed between the 234 and 238 isotopes of singly ionized uranium.

The emission spectrum of curium has been measured by Conway, Moore & Crane (24) in the region 2516 to 5000 Å; the wavelengths of the most prominent lines in the arc spectrum are tabulated, and technical details of methods of handling the highly radioactive curium samples in the spectrograph are given.

Magnetic measurements.—Earlier studies on the magnetic properties of the actinide elements are reviewed by Lister (81). A number of investigators have continued to examine the magnetic properties of uranium. Bates & Mallard (13) have redetermined the magnetic susceptibility of uranium metal. At 20°C., the susceptibility of pure uranium is $+1.740\times10^{-6}$ e.m.u. per gm. In the temperature range 20° to 350°C., the susceptibility (per gram) is given by the equation

$$\chi_U = 32 \times 10^{-11}\, T + 1.564 \times 10^{-6} + 24.0 \times 10^{-6}/T.$$

In the compound U_6Fe, the uranium is found to have a susceptibility of $+2.036\times10^{-6}$ e.m.u. per gm. at 20°C., which is practically temperature independent. The susceptibility of U^{+3} and U^{+4} compounds has been measured by Dawson (28). The tetravalent uranium compounds UF_4, UCl_4, and UBr_4 obey the Curie-Weiss law over the temperature range 77° to 550°K. The results indicate that the ion U^{+4} has the configuration $5f^2$. The trivalent compounds UCl_3, UBr_3, and UI_3 deviate from the Weiss-Curie law below about 350°K. The results are interpreted as arising from a $5f^26d^1$ electron configuration for the tri-iodide and tribromide; the assignment is not conclusive for the trichloride. Similar results are reported by Sacconi (104), who studied various diketone and nitroso compounds of U(IV). It is concluded that the

configuration of U^{+4} is $5f^2$. The situation with respect to U^{+4} is complicated by the results of Trzebiatowski & Selwood (131). These investigators measured the susceptibility of solid solutions of UO_2 in ThO_2, using the magnetic dilution technique introduced by Selwood. Since the moment at the greatest dilution is in agreement with the "spin-only" formula for two unpaired electrons, it is concluded that U^{+4} in UO_2 has the 6d rather than the 5f electron distribution. In an independent study, using measurements on undiluted material, Dawson & Lister (30) have studied the magnetic susceptibility of various uranium oxides. For UO_2, the magnetic moment indicates the configuration $5f^2$ (or possibly $5f^16d^1$) rather than a $6d^2$ for the U^{+4} ion. In UO, however, there appear to be unpaired electrons in 6d orbits. The interpretation of magnetic measurements on such magnetically concentrated systems remains open to question. The present evidence on the whole is that the U^{+4} ion has the $5f^2$ configuration.

The magnetic susceptibilities of CmF_3 and AmF_3 have been measured by Crane, Wallmann & Cunningham (26). The molar susceptibility of CmF_3 is found to be $-(22{,}500 \pm 4{,}000) \times 10^{-6}$ c.g.s. units at 295°K., and agrees within experimental error with that theoretically expected for a $5f^7$ configuration. The susceptibility of AmF_3 is found to agree with a $5f^6$ configuration for Am^{+3}, and a multiplet splitting between the $^7F_0$ and $^7F_1$ states comparable to kT, but greater than in the case of Eu^{+3}. These results are thus in agreement with an actinide series hypothesis.

Actinium

The element actinium has been isolated in pure form for the first time by Hagemann (56). Unlike previous attempts which involved extraction of the minute equilibrium amounts of actinium from naturally occurring radioactive minerals, Hagemann obtained actinium by nuclear transformation of radium:

$$Ra^{226}(n, \gamma)Ra^{227};\ Ra^{227} \xrightarrow[\text{short}]{\beta^-} Ac^{227}.$$

Milligram amounts of actinium were then isolated by a solvent extraction method. Yang (151) has effected the separation of actinium from large amounts of lanthanum by ion exchange, using ammonium nitrate as the eluent. Fried, Hagemann & Zachariasen (46) have prepared a considerable number of pure actinium compounds and identified and characterized most of them by x-ray crystallographic methods. All of the identified actinium compounds are isostructural with the corresponding lanthanum compounds; Ac^{+3} is the largest and most basic of the known +3 ions.

Thorium

The chemistry of thorium appears to be attracting increasing attention. Buyers & Audrieth (21) have made an extensive investigation of phosphates and polyphosphates of thorium and indicate the utility of these compounds

for separation from rare earths. Asselin, Audrieth & Comings (11) have studied the separation of thorium and rare earths by solvent extraction; extraction of thorium with *n*-butanol from thiocyanate solution appears to be effective. Templeton & Hall (124, 125) have also examined the applicability of solvent extraction for thorium-rare-earth separations and find that higher alcohols and ketones will preferentially extract thorium from rare-earth nitrates. The general behavior of thorium in organic solvents has been discussed by Yaffe (149) and Templeton & Hall (123).

One of the most interesting recent developments in thorium chemistry is the report of Anderson & D'Eye (7) on the preparation of lower oxidation states of thorium. By reducing ThI_4 with thorium metal at 450° to 550°C., Anderson & D'Eye obtained ThI_3 and ThI_2; these compounds were characterized by their x-ray diffraction patterns and by chemical means. The lower iodides of thorium appear analogous in every respect to the corresponding hafnium and zirconium compounds.

The solution chemistry of thorium has been the subject of several investigations. Kurbatov and co-workers (79, 80) have studied the behavior and precipitation characteristics of thorium (IV) in very dilute solution. Kraus & Holmberg (76) have continued their intensive investigation of the hydrolytic behavior of metal ions with a study of the acidity of thorium tetrachloride solutions. Th(IV) hydrolyzes in a manner qualitatively different from U(IV) and Pu(IV) and yields ThO^{++} directly, which then undergoes extensive polymerization. Kraus & Holmberg feel that the differences are greater than might be anticipated if all three elements were actually members of one transition series. Day & Stoughton (32) have determined the equilibrium constants for the formation of complex ions of Th^{+4} with anions of the hydrochloric, nitric, chloric, bromic, hydrofluoric, and the chloracetic acids; this work marks an important advance in our knowledge of thorium chemistry. Using spectrophotometric techniques, Moeller & Kobisk (88) have studied complex formation between thorium ion and 2,5-dihydroxyquinone; a 1:1 complex, probably of a chelate structure, was shown to form in methanol solution. The behavior of thorium and uranium compounds in liquid ammonia has been studied by Watt, Jenkins & McCuiston (138). Treatment of hydrated thorium nitrate with liquid ammonia apparently yields hydrated thorium oxide, while thorium sulfate under similar conditions is converted to a basic sulfate of thorium. Thorium iodate and oxalate 2-hydrate are unreactive to liquid ammonia and are only very slightly soluble. Winter (148, 145) has reported preliminary experiments on the exchange of O^{18} with ThO_2; moderately rapid exchange is observed at 350°C.

The crystal structures of a number of thorium compounds have been reported during the period under review. Pabst (94, 95) describes a new monoclinic thorium silicate mineral $ThSiO_4$, isostructural with monazite. D'Eye (34) has found $ThBr_4$ to be body-centered tetragonal (space group D_{4h}^{19}-I4/amd); like the chloride, the bonds are partially covalent in character. The thorium-boron system has been quite thoroughly investigated (19) by x-ray

methods. Two intermediate phases, ThB_4 and ThB_6, have been identified. ThB_4 appears to have a melting point well above 2,500°C. A similar study of the thorium-sulfur system has been carried out (36). The phases ThS, Th_2S_3, Th_7S_{12} and ThS_2 have been identified, and many of their properties studied. Hunt & Rundle (65) have shown that ThC_2 is not tetragonal as previously reported, but is instead C-centered monoclinic (space group C_2/c or Cc). The structure contains C_2 groups, and considerable covalent character for the Th-C bonds is indicated.

Only one thermochemical investigation on thorium compounds has been reported. Eyring & Westrum (40), by determining the heat of solution of thorium metal in hydrochloric acid, find the heat of formation of $ThCl_{4(c)}$ to be −284.5 kcal. per mole at 25°C., markedly lower than the value reported in the previous literature.

Protactinium

Since protactinium is in many ways the least studied of the actinide elements, any new chemical results are of considerable interest for the comparative chemistry of the actinide elements. Such results are now becoming available. Katzin, Van Winkle & Sedlet have analyzed various residues (72) obtained from uranium ore processing for their protactinium content and succeeded in extracting milligram amounts of the element in pure form. Maddock & Stein (85) have discussed solvent extraction procedures for extracting protactinium and indicate a method of separation based on adsorption on MnO_2 followed by solvent extraction of protactinium-cupferron complex (84). An important advance is the application of ion exchange methods for isolation and for the study of ionic species in solution. Kraus & Moore (77) find that Pa(V) can be readily absorbed by anion exchange resins from hydrochloric acid solution or from hydrofluoric-hydrochloric acid solutions, and they find that excellent separations of protactinium from niobium and tantalum can be effected in this way, at least on the tracer scale. Yang (150) has also studied the separation of protactinium from tantalum by ion exchange resins.

The solution chemistry of protactinium remains for the most part a mystery. Maddock & Miles (83) have carried out a tracer investigation and conclude that aqueous solutions of Pa(V) resemble those of zirconium more closely than those of tantalum. Haissinsky & Yang (62) have studied the stability of oxalate, citrate, and tartrate complexes of zirconium and tantalum and believe that from these results it is possible to predict the properties of the complex ions of protactinium.

A significant contribution to protactinium chemistry are the results of Elson, Fried, Sellers & Zachariasen (37). Although lower oxidation states of protactinium have been reported by several workers (152, 17), Elson *et al.* have succeeded in unequivocally establishing the existence of a +4 state by preparing and identifying $PaCl_4$ and PaO_2. The tetrachloride has the tetragonal UCl_4-type structure. The existence of Pa_2O_5 was also established, and

the existence of a series of solid solutions between PaO_2 and Pa_2O_5 shown. The oxide stable on ignition in air, however, is found to be $PaO_{2.25}$.

Uranium

As might be expected, not only from its comparatively ready availability, but because of its diversified chemistry, the number of publications dealing with uranium chemistry probably exceeds those dealing with all of the other actinide elements. Exclusive of work directly concerned with analytical methods, which are not discussed here, principal interest has been in the solution chemistry of uranium in both water and organic solvents.

Uranium metal.—Rosen has described an electrolytic method for the preparation of uranium metal from UF_4 baths at elevated temperatures (103a). Newton (91) has indicated the usefulness of metallic uranium in purifying the rare gases, a procedure which is feasible because of the very high reactivity of uranium metal at elevated temperatures with all of the impurities commonly present. The physical properties of uranium metal have received some investigation. Thus, Allendörfer (5) reports a melting point for uranium of $1{,}090 \pm 2$°C., but this value is about 40° lower than the commonly accepted U. S. Bureau of Standards value of 1,132°C. Tucker (132) has been able to work out an approximate crystal structure for the β phase of metallic uranium (stable between 660° and 760°C.). The unit cell is tetragonal ($a_0 = b_0 = 10.52$ Å, $c_0 = 5.57$ Å) and contains 30 atoms. The low symmetry and complexity of the structure accounts for the hard, brittle nature of the phase. Finally, Goodman & Shoenberg (53) report that uranium metal becomes a superconductor at temperatures ranging from 0.75° to 1.3°K.

The intermetallic systems of uranium have received attention. Pfeil (100) has described the uranium-molybdenum alloy system in detail, and Grogan (55) has done the same for the uranium-iron system. Both of these alloy systems are complex. The crystal structures of compounds of uranium with manganese, iron, cobalt, and nickel have been given by Baenziger *et al.* (12), and considerable material of interest from the structural point of view is presented by them.

Uranium-oxygen system.—Sheft, Fried & Davidson (111) have described a convenient method for the preparation of UO_3 by treating lower uranium oxides at 450° to 750°C. with oxygen at 30 to 150 atm. pressure. Boullé *et al.* (18) have studied the thermal decomposition of uranyl oxalate as a source of UO_2, but the reviewers question the validity of their results. Watt *et al.* (137) describe the preparation and properties of uranium peroxide; quantitative precipitation of $UO_4 \cdot 2H_2O$ occurs at pH 2.5 to 3.5. The constitution of the uranates of sodium has been studied by Wamser *et al.* (134) who find that $Na_2U_7O_{22}$ and $Na_6U_7O_{27}$ (or mixtures thereof) are obtained when uranium is precipitated from uranyl nitrate solutions by sodium hydroxide. The reactions of anhydrous uranium oxides with liquid N_2O_4 have been studied by Gibson & Katz (50); UO_3 reacts readily to yield $UO_2(NO_3)_2 \cdot 2NO_2$.

The dielectric properties of UO_2, U_3O_8, and UO_3 have been investigated by Freymann & Freymann (42). In the radiofrequency range, the behavior of the three oxides is markedly different. The results are interesting but are difficult to interpret because of uncertainties in the composition of the oxides. The most important paper in recent years on the oxides of uranium is that of Alberman & Anderson (4). These investigators have studied the phase relations of compositions in the vicinity of UO_2. Disproportionation of homogeneous into heterogeneous phases is found to occur on heat treatment. These observations may do much to reconcile contradictory results obtained by tensimetric and x-ray methods of study. The coefficients of expansion of mixtures of U_3O_8 and UO_2 have been determined by Day (31). Like much work on uranium oxides, it suffers from uncertainties in the composition of the oxides used. Magnetic studies on UO_2 have been discussed above.

Uranium halides.—Fried & Davidson (44) have discovered a new synthesis for UF_6 not involving the use of elemental fluorine (58). The reaction of UF_4 with O_2 at 800°C. proceeds according to the following equation:

$$2UF_4 + O_2 \rightarrow UF_6 + UO_2F_2.$$

It is thus possible to prepare UF_6 without recourse to fluorine. The preparation and properties of another so-called intermediate uranium fluoride, U_4F_{17}, has been reported by Agron & Weller (2); it is prepared by treating UF_4 with UF_6 vapor. The reduction of UF_6 by hydrogen has been reinvestigated by Dawson *et al.* (29), who find, as have others, that although the reduction of UF_6 by hydrogen should proceed to completion on thermochemical grounds, nevertheless in practice only partial reduction is observed even at elevated temperatures. The reduction of UF_6 by H_2 for some unknown reason has an unusually high heat of activation. The molecular structure of UF_6 has been discussed by Fumi & Castellan (47) and by Bauer (14).

Relatively little of importance has appeared on the other halides of uranium. The preparation of uranium halides from uranium hydride and halogen or halogen acid is described by Johnson & Newton (66), the preparation of higher chlorides of uranium by Reiber (102), and the preparation of UI_3 by Holmes (64).

Other binary uranium compounds.—Warf (135, 136) has given a very complete and authoritative description of the preparation, properties, and reactions of uranium hydride, UH_3. The crystal structure and phase relationships of the uranium (and thorium) carbides UC and UC_2 are given detailed discussion by Wilhelm *et al.* (147), and practical details of producing uranium carbides are disclosed by Carter & Daane (22). The complex uranium-sulfur system has been investigated by Eastman *et al.* (36); the compounds US, U_2S_3, and US_2 were shown to exist, but the phase relationships are not as fully worked out as for the corresponding thorium compounds. The uranium-boron system (19) has also been studied (see thorium-boron system under THORIUM). There are three intermediate phases, UB_2, UB_4, and UB_{12}, so far characterized in the uranium-boron system. The synthesis of uranium com-

pounds of sulfur, selenium, tellurium, nitrogen, phosphorus, arsenic, carbon, or boron through the intermediary UH_3 is described by Newton & Johnson (92).

Uranium ions in aqueous solution.—The ionic species of U(IV) in perchloric acid and sulfuric acid solution have been studied by Betts & Leigh (15). On the basis of extraction of U(IV) by thiophenoyltrifluoracetone (thenoyltrifluoracetone), it is concluded that U^{+4} is the predominant species in perchloric acid; in sulfuric acid at least two complex species $U(SO_4)^{++}$ and $U(SO_4)_2$ are present. Kraus & Nelson (78) also find that U^{+4} is the important species in acid solution. The acidity constant for the reaction

$$U^{+4} + 2H_2O \rightleftarrows UOH^{+3} + H_3O^+$$

was found to be $K_a = 0.21 \pm 0.02$. The chemistry of U(V) ions has been amplified by an investigation of the U(IV)-U(V)-U(VI) equilibrium in perchloric and hydrochloric acids by Nelson & Kraus (90). The equilibrium constant $K.^\circ_{eq.}$ for the reaction

$$2UO_2^+ + 4H_3O^+ \rightleftarrows UO_2^{+2} + U^{+4} + 6H_2O$$

was determined to be $(1.7 \pm 0.3) \times 10^6$, and the stability constant of the U(VI) complex ion UO_2Cl^- was found to be 2.4. By measuring the rate of disproportionation of U(V) in deuterium oxide by a polarographic method, Duke & Pinkerton (35) conclude that the disproportionation reaction very likely proceeds by an hydroxyl transfer mechanism rather than one involving a hydrogen atom transfer. That this is indeed reasonable may be inferred from the interesting results of Rona (103) on the kinetics of uranium exchange between the IV and VI states. Here also oxygen transfer is invoked to account for the observed phenomena. The hydrolysis of uranyl ion UO_2^{++} in aqueous solution leads to the formation (122) of the ions $U_2O_5^{++}$, and $U_3O_8^{++}$ and not $UO_2(OH)^+$ and $UO_2(OH)_2$. Similar results are found in uranyl sulfate solution (8). Spectrophotometric methods have been used to study complex ion formation in uranyl nitrate and sulfate solutions, and the instability constants for UO_2SO_4 and $UO_2(NO_3)^-$ have been measured by Betts & Michels (16).

Marshall *et al.* (86) have made a detailed study of the uranyl nitrate-water system above 60°C.; uranyl nitrate trihydrate is shown to have an incongruent melting point at 113°C. and the dihydrate to have a stable melting point at 184°C. These results are in contradiction to the older information in the literature, but are probably more reliable. The activity coefficient of uranyl nitrate in sodium nitrate solution has been measured by a solvent extraction technique (52). Secoy (110) has extended earlier results on the uranyl sulfate-water system up to the critical temperature of water and has been able to give a comprehensive phase diagram for this system.

The complex ions of uranium continue to attract interest. As mentioned above, there is considerable new information available on complex species in

aqueous solution. In addition, Feldman & Neuman (41) have shown that there are two citrate complexes of UO_2^{++} in the pH range 2.0 to 3.64. Ahrland (3) has shown that no polynuclear complexes occur in the uranyl thiocyanate system.

Uranium in nonaqueous solvents.—The phenomena and underlying bases for the solubility of uranyl salts in organic solvents have been responsible for considerable research. DeKeyser *et al.* (33) have measured the solubility of uranyl nitrate in various ethers, esters, alcohols, and ketones, with particular emphasis on the water-uranyl nitrate-ethyl acetate system. The heats of solution of uranyl nitrate hydrates in water and organic solvents have been measured by Katzin, Simon & Ferraro (71), who point out that the heats of solution are largely influenced by the base strength of the solvent. Kaplan *et al.* (68) have measured the absorption spectra of uranyl nitrate in various organic solvents. Differences in the spectra taken in various solvents are interpreted in terms of series of nitrate complexes UO_2^{++}, $UO_2(NO_3)^+$, $UO_2(NO_3)_2$, and $UO_2(NO_3)_3^-$, the relative concentrations of which depend on the nature of the solvent. The stable trinitrato uranyl ion $UO_2(NO_3)_3^-$ is responsible for the enhancement of uranyl nitrate extraction into methyl isobutyl ketone by hydrazine or quaternary ammonium salts (69). Furman *et al.* (48) discuss the extraction of aqueous uranyl nitrate by diethyl ether in great detail.

A number of organic complex compounds of uranyl nitrate have been prepared and characterized. Mathieson (87) has prepared ketone and ether complexes of uranyl nitrate; the acetone and methyl ethyl ketone complexes were shown to have the general formula $UO_2(NO_3)_2 \cdot 3H_2O \cdot$ ketone. Watt & Machel (139) also prepared a methyl isobutyl ketone co-ordination compound of uranyl nitrate. Their product is anhydrous and has the composition $UO_2(NO_3)_2 \cdot C_6H_{12}O$, and the fact that it is anhydrous rather than a hydrated compound as obtained by other workers is attributed to the use of $UO_2(NO_3)_2 \cdot 2H_2O$ as the starting compound. Watt & Machel were unable to obtain complex compounds with urea, thiourea, guanidine, nitrilotriacetic acid, and ethylenediamine tetracetic acid, but did obtain compounds with hexamethylene tetramine and ethylenediamine. Mueller (89) has successfully prepared uranyl 2-ketodiacetone-gluconate and uranyl diethyl citrate. Soye (113) has reported the preparation of a complex choline compound $[UO_2(NO_3)_2 \cdot C_5H_{15}O_2N]_n$. The preparation of anhydrous uranyl acetylacetone is described by Abrahamson & Brown (1).

Miscellaneous.—Freymann *et al.* (43) have studied the absorption spectra of UCl_4 and UBr_4 and propose a classification of their absorption bands in the visible region involving the vibration frequencies of these molecules. Pant (97) has made a spectrographic analysis of the absorption and fluorescence spectra of uranyl sulfate and uranyl fluoride according to a method devised by the author previously. Gordon (54) has used the luminescence spectra of crystals and solutions of uranyl sulfate to study the nature of uranyl sulfate solutions. An extensive survey of the optical crystallography

of uranium compounds is given by Staritzky & Truitt (115). Sundberg & Sillén (121) have made an analysis of the crystal structure of KUO_2VO_4 which the authors call synthetic anhydrous carnotite. This crystal consists of layers of $UO_2VO_4^-$ separated by sheets of K^+. A considerable number of papers dealing with minerals of uranium have appeared recently but they are not considered here.

Neptunium

There has been relatively little new work published in the last year on neptunium chemistry, no doubt a result of the difficulties encountered in obtaining macro amounts of the long-lived Np^{237}. This situation is regrettable for in many respects the chemistry of neptunium is of great scientific interest. Thus it is almost unique in possessing a stable +5 oxidation state in aqueous solution in the form of the simple ion NpO_2^+. Some new work has, however, appeared. Westrum & Eyring (141) have found the melting point of neptunium metal to be 639.5°C. and a measured density ranging between 16.9 to 20.1 gm. per cc. The heat capacity and entropy of NpO_2 has been determined by Westrum, Hatcher & Osborne (143) although final results are not yet available. Fried & Davidson (45) describe the preparation of NpF_3 from NpF_4 by treatment with a mixture of hydrogen and hydrogen fluoride.

Hindman has continued his investigations into the solution chemistry of neptunium. An examination of the polarographic behavior of the Np(III)-Np(IV) couple in chloride and perchlorate solution is of interest (63). The couple is polarographically reversible in hydrochloric acid with an oxidation potential of -0.142 ± 0.005 v. The couple is, however, polarographically irreversible in perchlorate media. Hindman (112) has also devoted considerable attention to the spectrophotometry of neptunium solutions. The spectra of Np(III), Np(IV), Np(V), and Np(VI) have been determined in 1 *M* $HClO_4$. The fine-structure is interpreted as being due to symmetrical metal-oxygen vibrations in ions of the type NpO_2^{++} and NpO_2^+. The vibrational frequency of the Np(V) ion is 753 $cm.^{-1}$ and for Np(VI), 715 $cm.^{-1}$ in 1 *M* $HClO_4$.

Plutonium

Peppard & co-workers (99) have isolated microgram amounts of Pu^{239} from Belgian Congo pitchblende concentrates. About 7.0 ± 0.7 parts Pu^{239} in 10^{12} parts of concentrate (45.3 per cent uranium) were found. This value implies a neutron source additional to that produced by spontaneous fission of uranium.

Kraus & Nelson (78) find the acid constant of Pu(IV) to be almost identical with that of U^{+4}. The close resemblance between U^{+4} and Pu^{+4} leads Kraus & Nelson to the conclusion that these two elements are members of a rare-earth-like series. Schlyter & Sillén (105) have studied the coprecipitation of Pu(IV) with LaF_3 and conclude that PuF_4 is probably the species which is carried with LaF_3 in the form of anomalous mixed crystals. Finally, Westrum & Wallmann (144) have found the melting point of PuF_3 to be

1,426 ± 2°C. with a heat of sublimation of 89 kcal. per mole at 1,400°C. An equation for the dissociation pressure valid from 1,200 to 1,660°K. was also obtained.

Preparation of Heavier Plutonium Isotopes and Transplutonium Isotopes by Neutron Irradiation of Pu^{239}

A development of importance for large scale production of transplutonium elements was the announcement in 1950 that Pu^{240}, Pu^{241}, and Am^{241} are formed in significant quantities by the following series of reactions (49).

$$Pu^{239}(n, \gamma)Pu^{240}(n, \gamma)Pu^{241} \xrightarrow{\beta^-(10\ \text{years})} Am^{241}.$$

With the high fluxes available in chain-reacting piles, it is relatively easy to produce milligram amounts of Am^{241} by prolonged irradiation of Pu^{239}. Am^{241} in turn captures neutrons with a cross section such that it is possible to produce substantial quantities of Cm^{242} via the reactions

$$Am^{241}(n, \gamma)Am^{242} \xrightarrow{\beta^-(17\ \text{hr.})} Cm^{242}.$$

The availability of relatively large amounts of Am^{241} and Cm^{242} produced in this way not only has facilitated the study of americium and curium chemistry, but also made possible the production and discovery of elements 97 and 98 by transmutations involving Am^{241} and Cm^{242} as starting materials (see section on Berkelium and Californium below).

Americium and Curium

The first isolation of americium in the form of pure compounds is described by Cunningham & Asprey (27). The half life of Am^{241} is found to be 490 ± 14 years. The preparation and properties of americium metal are described by Westrum & Eyring (142) who reduced AmF_3 with barium in a BeO crucible. The metal has an abnormally low density, resembling europium metal in this respect. The vapor pressure of americium metal has been measured by Simpson & Erway (39) from dilute solution in plutonium. The vapor pressure in the temperature range 1,450° to 1,820°K. is given by the equation $\log_{10}P_{mm} = 7.02 - (11{,}300)/T$ to within a factor of two or three. Broido & Cunningham (20) have studied the vapor phase hydrolysis of $AmCl_3$. The heat of reaction was found to be 23.0 kcal. per mole and the entropy change $\Delta S_{298°K.} = 36.7$ e.u. per mole.

The heat of formation of the Am^{+3}(aq) ion is found by Lohr & Cunningham (82) to be -161.3 ± 1.4 kcal. per mole. The calculated value for Am^{+4}(aq) is -112.2 kcal. per mole; the heats of formation of AmO_2^+(aq) and AmO_2^{++}(aq) have not been determined. The pentavalent state of americium has been prepared by Werner & Perlman (140) who obtained it by adding NaOCl to a K_2CO_3—Am(III) solution at 95°C. By analogy to neptunium and plutonium, Am(V) is expected to have the ionic form AmO_2^+. The disproportionation of Am(V) has been studied by Stephanou, Asprey & Penneman (116). The +6 oxidation state of americium has been obtained by

the same workers (10) by treating Am(III) solutions with ammonium peroxydisulfate. The existence of the +6 state was rendered certain by spectrophotometric means and by isolation of the compound $NaAmO_2(C_2H_3O_2)_3$, isostructural with the corresponding +6 compounds of uranium, neptunium, and plutonium. The autoreduction of AmO_2^{++} has been examined by Asprey & Stephanou (9). The absorption spectra of aqueous solutions and solid compounds of americium have been obtained (117). The potential of the Am(V)—Am(VI) couple in 1 *M* $HClO_4$ is found to be -1.600 ± 0.005 v.; the complexing effect of sulfate on americyl ion is about the same as for NpO_2^{++}(98).

An effective separation of americium and curium from rare-earth elements by ion-exchange resin methods has been described by Street & Seaborg (118). The isolation and properties of curium are described in great detail by Crane & Perlman (25). Curium metal has been prepared on the microgram scale by reduction of CmF_3 with barium metal vapors at 1,275°C. The metal is silvery and tarnishes more rapidly than americium or plutonium metals (133).

Berkelium and Californium

The discovery of elements 97 and 98 by Seaborg and co-workers is an important development in the chemistry of the actinide elements. Berkelium was discovered in December, 1949, by Thompson, Ghiorso & Seaborg (127, 128) as a result of irradiation of Am^{241} with 35-M.e.v. helium ions:

$$Am^{241}(\alpha, 2n)Bk^{243} \text{ [or possibly } Am^{241}(\alpha, n)Bk^{244}\text{]}.$$

This isotope (Bk^{243} or Bk^{244}) has a half life of 4.6 hr. and decays by electron capture with about 0.1 per cent branching decay by alpha-particle emission. The separation and chemical properties of berkelium have been described by Thompson, Cunningham & Seaborg (126). Berkelium is isolated by ion-exchange methods. It appears to exist in aqueous solution predominantly as Bk^{+3}, but it can be oxidized, presumably to the +4 state, by bromate, dichromate, or cerium(IV). The oxidation potential of the Bk(III)—Bk(IV) couple does not differ by more than 50 mv. from the Ce(III)—Ce(IV) couple. E_f would therefore appear (67) to be -1.62 ± 0.006 v. for the couple $Bk(III) \rightarrow Bk(IV) + e^-$.

Californium (atomic number 98) was first prepared by bombardment of Cm^{242} with 35-M.e.v. helium ions (129):

$$Cm^{242}(\alpha, 2n)Cf^{244}$$

Cf^{244} has a half life of about 25 min. and decays at least partially by the emission of 7.1-M.e.v. α-particles; a more detailed discussion of the preparation, radiations, and chemical properties of Cf^{244} is to be found in a later paper by Thompson, Street, Ghiorso & Seaborg (130). The most satisfactory method for isolating californium consists in selective elution from a cation exchange resin with ammonium citrate solution.

The behavior of americium, curium, berkelium, and californium on elution is considered by Street, Thompson & Seaborg (119) to provide strong evidence for considering berkelium and californium as the eighth and ninth members of an actinide series. This evidence consists of a break between berkelium and curium in the elution curve analogous to a similar break between terbium and gadolinium, indicating that the two series have strikingly analogous breaks in ionic radius at the midway point. Chemical information about californium is still meager. It appears to exist in aqueous solution predominantly as Cf^{+3}. No higher state has as yet been obtained, and it appears unlikely that such states will be found. Nevertheless, as the second element beyond the midpoint of an actinide transition series, the possibility of oxidation to a +5 state, CfO_2^+, cannot be excluded.

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ELECTROMAGNETIC SEPARATION OF STABLE ISOTOPES[1]

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Calutron Separation of Isotopes

In the fall of 1945 it became possible to examine the electromagnetic isotope separation equipment to see if it could be adapted to the separation of isotopes of elements other than uranium. In this way, improvements might be made in the calutron,[3] as the electromagnetic isotope separating equipment is called, in its main objective of processing uranium and, at the same time, enriched isotopes could be collected which might have value in fundamental or applied scientific research. This program is operated now almost entirely for the isotopes produced and the scientific findings which they make possible. The ultimate goal is to enrich each naturally occurring atomic species, or nuclide (110), in the periodic chart which is not already 100 per cent abundant (94, 95).

Fundamentally, there is little difference between a laboratory mass spectrometer and its production counterpart, the calutron. Both use electric fields for acceleration, magnetic fields for separation of isotopic ion species, and ion sources and collectors, all operating in a vacuum. The primary difference then is that the calutron is designed to collect useable quantities of desired isotopes, while the laboratory spectrometer is used almost entirely as an instrument for detection or analysis. Of course, if one desired, very small quantities of virtually any isotope could be collected in the laboratory instrument, but the collection rates would be exceedingly small. Figure 1 shows a schematic diagram of the calutron.

The electromagnetic separation of isotopes by the calutron involves the following phases: (*a*) preparation of suitable charge material for the calutron ion source, (*b*) operation of the calutron in separating the isotopes, (c) quantitative recovery from the collectors and chemical purification of the separated isotopes, (*d*) spectrochemical analysis of refined isotopes, and (*e*) preparation of suitable sample and mass spectrometer analysis of enriched isotopes.

[1] This review is essentially a survey of papers published in 1950.

[2] The author wishes to acknowledge the helpful suggestions of Russell Baldock, L. E. Burkhart, J. R. McNally, Jr., C. E. Normand, and Boyd Weaver. Particular appreciation is expressed to J. R. Patton for his authorial aid and to Edith Zarzecki for typing the manuscript.

[3] The term "calutron" is used to designate the production-type mass spectrographs, the word having been coined because these machines were developed at the University of California under E. O. Lawrence.

The flexibility which makes possible the electromagnetic separation of isotopes is derived primarily from the magnetic field which can be set at a predetermined value to focus ions of mass ranging from lithium to uranium at the collector. Also, ion accelerating and focussing voltages are variable.

Calutron Ion Sources

Calutron ion source units which had been designed and used for uranium isotope collections possessed a certain degree of flexibility as to temperature

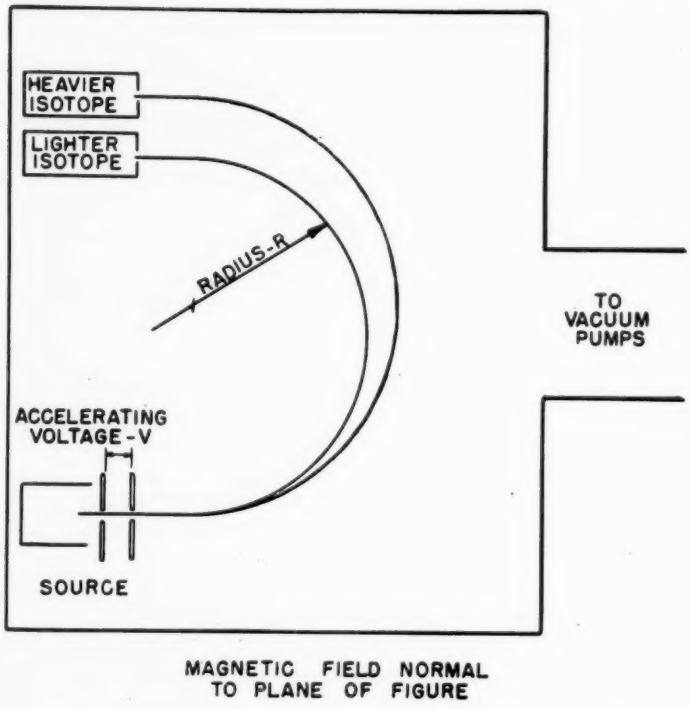

Fig. 1. Simplified diagram of the calutron isotope separator.

range, accelerating electrode arrangement, arc number and size, and cooling system, so that only minor modifications were necessary for the first several elements processed. In processing a variety of elements and compounds having widely varying vapor pressures, it has been necessary to develop source units operable over temperature ranges above and below the range available with sources previously developed. Tests on heater power inputs and various cooling arrangements indicated that the temperature range of uranium-type ion source units could be extended sufficiently to cover approximately half of the elements having more than one nuclide if the charge compound of the element under consideration was carefully chosen.

For charge materials occurring as liquids or gases at room temperature, sources were modified to use external charge feed, the flow of feed material to the arc being controlled by a sensitive needle valve. This innovation further increased the useful range of the uranium-type source unit.

Other elements, for example, the rare earths and the platinum group, required temperatures above the upper limit of the uranium-type source unit; hence, development of unique ion sources was begun. For such low vapor pressure materials requiring higher operating temperatures than available with standard source units, a special high temperature unit was developed.

Early in the program it was found that a small flow of gas such as nitrogen into the arc was beneficial, and with some elements necessary, for stabilizing the arc and promoting production. All source units were equipped for using support gas.

The problem of producing ions of all isotopes for calutron operation is not completely solved; however, methods and equipment now in use are adequate to produce ions, with varying degrees of efficiency, from virtually any element in the periodic chart.

Calutron Isotope Collectors

For each element processed, an isotope collector must be designed, providing properly spaced receptacles for whatever isotopes may be present. Isotope collector structural materials, structural design, and cooling, all required attention before a general isotope collection program could be successful. Since one mass unit separation at the collector decreases as the mass of the ions increase, each element requires especially designed collectors. In addition to this consideration, which is essentially a problem in pocket placement, suitable pocket materials and cooling techniques must be chosen in order to retain the deposited material. The temperature of receiving surfaces, which must necessarily be bombarded with ions, must be kept sufficiently low that deposited material will be retained and not lost to cooler surfaces such as walls of the vacuum chamber or through the vacuum system. The problem of building a collector for any element then consists of calculating proper pocket spacing for the desired isotopes, and from vapor pressure considerations, determining suitable pocket material and cooling techniques.

During the early part of the stable isotope separation program, modified uranium-type collectors were used while other designs and methods for fabrication were being developed. Design was dictated by the desire for the basic mechanism to have maximum flexibility in order that collectors could be constructed for any element from a minimum number of parts. The all-purpose type collector, in which any number of pockets up to 10 can be assembled at predetermined spacings, meets these objectives. The basic structure permits the placing of collectors to receive the isotopes of any element in the periodic chart; pockets may be replaced easily if desired, and cooling may be employed as required.

Collector materials vary with the element being processed, and the receiver parts may or may not be water-cooled, depending on the energy to be dissipated and the vapor pressure of the collected material. Furthermore, with some elements, special retention techniques have been required. Sulfur was allowed to combine chemically with copper shavings packed in the collector pocket.

Mercury was retained by allowing it to amalgamate with silver collector pockets, and by cooling the pockets with a circulating refrigerant (46). In

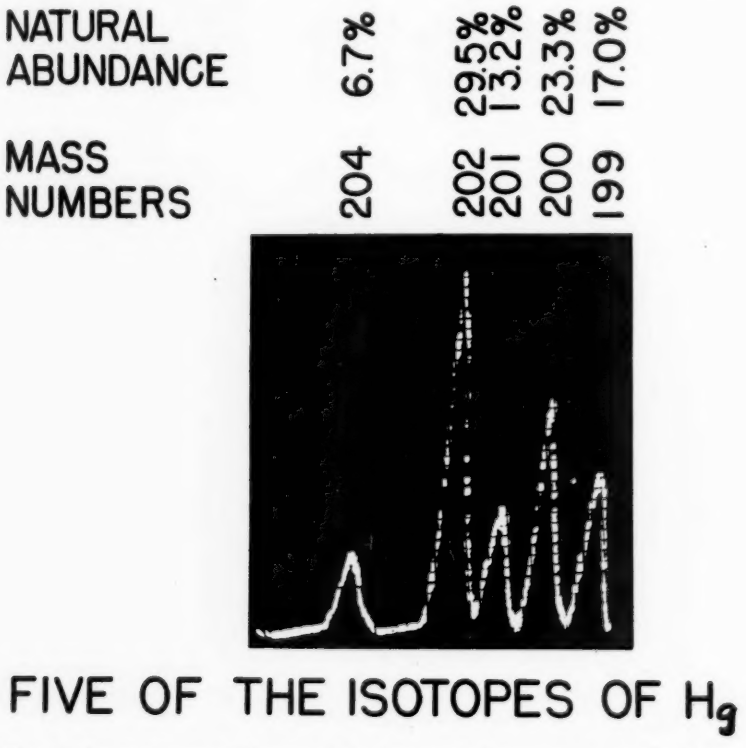

FIG. 2. An oscillogram of some of the isotopes of mercury as resolved by the calutron.

the processing of mercury, the problem of high vapor pressure in the calutron, and the contamination of collected isotopes by the condensation of neutral mercury vapor in the collector pockets, were solved by refrigerating the vacuum chamber. Figure 2 illustrates how effectively the isotopes of mercury can be resolved at the collector.

CHARGE MATERIALS FOR PRODUCTION OF IONS

The availability or synthesis of suitable calutron charge materials is essential. Several requirements must be met, such as suitable vapor pressure

at calutron operating temperatures, simplicity of molecular structure, stability of the compound and absence of water of crystallization. If the element itself has a suitable vapor pressure, it is generally used as charge material since its use greatly reduces extraneous ions or sidebands. For the same reason, simple compounds generally are preferred over the more complex compounds; thus, halides have been used widely. Anhydrous compounds are necessary because the water of crystallization gives rise to increased vacuum chamber base pressure and prolonged start-up time.

A wealth of basic inorganic chemistry has resulted from these charge material developments. Suitable charge materials of some 43 elements have been supplied for calutron separations of isotopes, including the synthesis of many unusual compounds and the development of methods of purification to meet special requirements.

The ultimate choice of the compound best suited for use in the electromagnetic separation of the isotopes of an element in the calutron is often made only after the systematic testing of a number of compounds. The ultimate criterion of suitability of such compounds is whether or not they give rise to a satisfactory rate of production of the separated isotopes of the given element. While a number of properties of the compounds are considered, chief consideration is usually the vapor pressure-temperature relationship, since such compounds must be sublimed into the arc chamber where positive ions are formed.

Recent mass spectrometer studies on a laboratory scale have led to a more satisfactory method for the evaluation of compounds. The compound under consideration is introduced into a mass spectrometer, and the ion current due to each of the fragments or species formed is plotted as a function of the mass of the fragment. This gives the relative abundance of the ions formed due to dissociation and ionization by the slow electrons used. The appearance potential is also determined for the singly charged metal ion involved.

It then follows that if the number of singly charged metal ions formed is a fair proportion of all of the positive ions thus produced from a compound, and if the appearance potential of the metal ions is not greatly in excess of the ionization potential of the metal, then the rate of positive ion production, and therefore the rate of production of the isotopes of the element in question, will be high.

Calutron Operational Procedures

After suitable ion sources, collectors, and charge materials have been assembled, the components are placed in an evacuated volume between the poles of an electromagnet. From this point, operational procedure is quite similar to that required for uranium separation. Metered ion currents at the collector are necessary to properly monitor the isotope beams and afford a means for estimating total isotope collection. Thus, for a singly charged ion, 1 amp.-hr. at the collector represents approximately 0.04 gm.-atom of the monitored isotope. The length of time allowed for a collection is determined

from the metered production rates on the desired isotopes, with some allowance for collector rejection and chemical losses.

By the end of 1950, sufficient calutron operational experience had been gained on most elements processed that full-scale isotope separation could begin almost immediately should the need arise.

Chemical Purification of Separated Isotopes

Upon receipt of collector pockets from the calutron operations area, the isotope contents are removed by one of several methods depending on the element and pocket material. Extreme care is exercised during this phase to prevent isotope contamination and to assure quantitative removal of the product isotope.

From this point, chemical purification procedures obviously vary widely, depending upon the element being processed. Reactions must be complete, filtrations or centrifugations must be carefully performed, and care must be exercised to minimize losses caused by discarding reaction side products.

At the beginning of 1951, adequate purification techniques had been worked out for every element which had been processed in the calutron. These included radioactive materials such as beryllium-10 and potassium-40, rare earths such as cerium, neodymium, and samarium, and toxic materials such as selenium and mercury.

More than 600 samples of enriched isotopes were chemically refined to make them suitable for use in isotope research. This was made possible by the development and adaptation of methods of quantitative separation of each of some 43 elements from all contaminants encountered in the electromagnetic separation process.

For example, the production of pure zirconium and hafnium fluorides was worked out. It was found that indium may be separated from gallium by the use of mandelic acid, $C_6H_5 \cdot CH(OH) \cdot (COOH)$. It was found that mandelic acid precipitates some of the rare earths and is useful in their separation. The physical and chemical properties of the mandelates of zirconium and hafnium were thoroughly investigated. Also, it was found that the homogeneous precipitation of the rare earths by hydrolysis of methyl oxalate is a selective process.

Furthermore, intensive research was necessary on methods for the chemical purification and analysis of uranium, rhenium, beryllium, indium, gallium, zirconium, and hafnium. Complexes of gallium and indium were supplied to aid the research of the Medical Division of the Institute of Nuclear Studies, and the hydrolytic properties of various organic salts were surveyed. A "quick freeze" technique was developed for the preparation of radiation sources of crystalline salts in their application to the preparation of K^{40} samples for use in the scintillation counter.

Chemical and Mass Analysis of Separated Isotopes

Upon completion of chemical purification, product isotopes are subjected

to chemical and mass analyses. Suitable standards have been determined for spectrochemical analyses for the common impurities and the burning of a standard sample on the same plate with the isotope sample permits plate correction. Impurity concentrations are determined by densitometering corresponding line intensities.

A sensitive spectrochemical method has been developed for handling a low ash type of filter paper containing micro amounts of beryllium; a low limit of 0.001 μg. beryllium has been obtained in a 1-inch filter paper. In addition, analysis methods for hafnium and other impurities in zirconium materials have been developed using pyroelectric methods (186).

Methods for handling small samples of precious isotope materials are

TABLE I

MASS ANALYSIS OF A COLLECTION OF CHROMIUM ISOTOPES

	Natural Abundance	Cr^{50} Pocket	Cr^{52} Pocket	Cr^{53} Pocket	Cr^{54} Pocket
Cr^{50}	4.49%	73.76±0.5%	0.26±0.13%	0.64±0.26%	1.8±0.2%
Cr^{52}	83.78	22.67±0.5	99.14±0.50	10.15±0.10	31.6±0.5
Cr^{53}	9.43	2.48±0.4	0.37±0.18	88.59±0.38	5.6±0.5
Cr^{54}	2.30	1.09±0.4	0.23±0.12	0.62±0.25	61.0±1.0

being continuously improved. Complete spectrographic analyses are presently carried out on a semi-quantitative basis on samples of the order of a milligram. Spectrum line enhancement is produced by a dilution of the isotope material in graphite powder.

In mass spectrometry, experience and development have made it possible to mass analyze isotope collections from all elements thus far processed in the calutron. More than 700 samples of isotopes of elements were prepared as compounds suitable for mass analysis. Table I summarizes a typical isotope analysis and shows what was collected in each collector pocket. Figure 3 is a typical page from the inventory records which carries over into the catalogue of stable isotopes, so interested researchers will know what is available for loan.

The interest in using certain stable isotopes as tracers has stimulated the development of microwave methods for isotopic analyses (93). The resolution of the microwave spectrometer is so great that theoretically there is room for more than 50 million rotational lines in the present experimental region. Although considerable progress has been made, isotopic analysis by microwave techniques do not yet meet the high precision of a Nier-type mass spectrometer. Routine results for carbon (155) and nitrogen (187) analysis, two important elements in biological studies, by microwave methods would be

1.00 ± 0.02 as compared with 1.000 ± 0.003 for a Nier-type mass spectrometer.

Isotopes Enriched Electromagnetically from January 1, 1946, to December 31, 1949

Sufficient progress had been made to collect 154 isotopes of 39 elements during the four-year period from January 1, 1946, to December 31, 1949.

Natural Isotopic Abundance:
K 39—93.38%
*K 40— 0.012%
K 41— 6.61%

Potassium
Atomic No. 19

Electromagnetically Concentrated Isotopes

Isotope	Series	Sample	Abundance of Enriched Isotope (per cent)	Available for Shipment	
				Element Weight (milligrams)	Product Form
K 39	W	67(a)	99.93	0	
K 39	BJ	237(a)	99.5	1,592	$KClO_4$
K 39	CM	346(ar)	99.9	9,920	KCl
K 39	DA	407(a)	99.94	19,418	K_2SO_4
K 39	DB	410(a)	99.74	5,659	KCl
K 39	DT	494(a)	99.89	9,374	KCl
K 40	W	68(a)	0.16	0	
K 40	BJ	238(a)	0.40	0	
K 40	CM	347(ar)	0.17	288	KCl
K 40	DA	408(a)	1.31	0	
K 40	DB	411(a)	0.40	124	KCl
K 40	DB	411(ar)	0.40	182	KCl
K 40	DT	495(a)	7.13	0	
K 40	DT	495(b)	8.1	0	
K 41	W	69(a)	88.36	0	
K 41	BJ	239(a)	92.9	65	$KClO_4$
K 41	CM	348(a)	86.8	0	
K 41	DA	409(a)	95.45	0	

* Radioactive.

FIG. 3. A typical page of the stable isotope inventory. All collections are shown even though some are exhausted, being on loan to various research laboratories.

These elements are shown in Table II; the number of isotopes and isotope samples are also indicated.

TABLE II

ELEMENTS PROCESSED IN THE CALUTRON JANUARY 1, 1946, TO DECEMBER 31, 1949

Element	Number of Isotopes	Number of Collections	Element	Number of Isotopes	Number of Collections
Lithium	2	16	Bromine	2	2
Beryllium*	1	3	Strontium	4	7
Boron	2	4	Zirconium	5	23
Carbon	2	2	Molybdenum	7	15
Nitrogen	2	1	Silver	2	6
Oxygen	3	2	Cadmium	8	17
Magnesium	3	13	Indium	2	12
Silicon	3	10	Tin	10	51
Sulphur	4	5	Antimony	2	4
Chlorine	2	5	Tellurium	8	24
Potassium	3	18	Barium	7	9
Calcium	6	23	Lanthanum	2	2
Titanium	5	5	Cerium	4	11
Chromium	4	9	Tungsten	4	11
Iron	4	130	Rhenium	2	2
Nickel	5	22	Mercury	7	165
Copper	2	10	Thallium	2	22
Zinc	5	10	Lead	4	18
Germanium	5	5	Uranium	3	9
Selenium	6	25			
Total Number of Elements Processed				39	
Total Number of Isotopes Processed				154	
Total Number of Samples Collected				728	

* To separate radioactive Be^{10}, artificially produced.

ISOTOPES PROCESSED FROM JANUARY 1, 1946, TO DECEMBER 31, 1950

By December 31, 1950, a total of 43 elements comprising 177 isotopes had been separated in the calutron in milligram to multigram quantities.

Table III summarizes not only the total number of elements and isotopes which have been processed in the calutron from January 1, 1946, to December 31, 1950, but shows also the isotopic purity which has been attained. Higher isotopic purities can be reached for many of the isotopes listed if the importance of the product warrants it.

SUMMARY OF ISOTOPES PRODUCED AND SHIPPED FROM JANUARY 1, 1946, TO DECEMBER 31, 1950

The tabulation in Table IV summarizes the stable and natural isotopes enriched in the calutron, the elements involved, the individual isotopes, the

TABLE III

Isotopes Processed and Isotopic Enrichments Attained in the Calutron January 1, 1946 to December 31, 1950

Element	Isotope Mass	Natural Abundance Per Cent (72, 78, 119, 123, 138, 179, 181, 203)	Enriched Abundance Per Cent (98)
Lithium	6	7.39	99.4
	7	92.61	99.91
Boron	10	18.83 (86, 87)	*
	11	81.17	*
Carbon	12	98.9 (163)	99.99
	13	1.1	7.52
Nitrogen	14	99.62 (163)	*
	15	0.38	*
Oxygen	16	99.757 (163)	*
	17	0.039	*
	18	0.204	*
Magnesium	24	78.60 (79)	99.5
	25	10.11	92.33
	26	11.29	98.12
Silicon	28	92.28 (86, 87,	99.4
	29	4.67 162)	68.6
	30	3.05	63.9
Sulphur	32	95.06	97.9
	33	0.74	5.54
	34	4.18	20.65
	36	0.016	0.319
Chlorine	35	75.4	92.4 (29)
	37	24.6	65.6
Potassium	39	93.3 (79, 163)	99.94
	40	0.011	7.13
	41	6.7	98.94
Titanium	46	7.95	84.26
	47	7.75	82.05
	48	73.45	99.23
	49	5.51	77.62
	50	5.34	84.69
Calcium	40	96.96	99.97
	42	0.64	61.4
	43	0.15	59.9
	44	2.06	96.2
	46	0.0033	4.8
	48	0.19	83.9
Vanadium	50	0.25 (77, 122)	**
	51	99.75	**
Chromium	50	4.49	73.76
	52	83.78	99.1
	53	9.43	92.1
	54	2.30	83.1
Iron	54	5.81	87.9
	56	91.64	99.10
	57	2.21	77.6
	58	0.34	86.0 (100)
Nickel	58	67.76	99.3
	60	26.16	97.7
	61	1.25	80.4
	62	3.66	94.7
	64	1.16	97.4
Copper	63	69.09 (38, 39)	99.7
	65	30.91	98.16
Zinc	64	48.89	93.4
	66	27.81	93.79
	67	4.07	62.6
	68	18.61	95.47
	70	0.620	48.4
Gallium	69	60.2	98.42
	71	39.8	98.08
Germanium	70	20.55 (80, 81)	88.1
	72	27.37	89.2
	73	7.61	68.9
	74	36.74	95.2
	76	7.67	79.3
Selenium	74	0.87	14.1
	76	9.02	57.4
	77	7.58	58.4
	78	23.52	82.5
	80	49.82	94.6
	82	9.19	52.36
Bromine	79	50.5	90.54 (29)
	81	49.5	96.81
Rubidium	85	72.8 (164)	95.97
	87	27.2	89.62
Strontium	84	0.56	63.68
	86	9.86	89.02
	87	7.02	73.1
	88	82.56	99.67
Zirconium	90	51.46	98.00
	91	11.23	86.89
	92	17.11	92.7
	94	17.40	92.8
	96	2.80	89.48
Molybdenum	92	15.86	95.5
	94	9.12	79.1
	95	15.7	88.0

TABLE III (*Continued*)

Element	Isotope Mass	Natural Abundance Per Cent (72, 78, 119, 123, 138, 179, 181, 203)	Enriched Abundance Per Cent (98)
Molybdenum	96	16.5	90.5
	97	9.45	77.97
	98	23.75	96.3
	100	9.62	93.0
Silver	107	51.35	98.96
	109	48.65	99.54
Cadmium	106	1.215	32.9
	108	0.875	24.8
	110	12.39	70.0
	111	12.75	64.5
	112	24.07	83.5
	113	12.26	54.1
	114	28.86	94.2
	116	7.58	71.2
Indium	113	4.23	65.4
	115	95.77	99.92
Tin	112	0.90	45.5
	114	0.61	24.1
	115	0.35	12.1
	116	14.07	76.3
	117	7.54	75.3
	118	23.98	91.8
	119	8.62	78.5
	120	33.03	95.4
	122	4.78	70.7
	124	6.11	83.1
Antimony	121	57.25	99.4
	123	42.75	96.8
Tellurium	120	0.091	22.3
	122	2.49	86.24
	123	0.89	60.91
	124	4.63	83.9
	125	7.01	87.9
	126	18.72	95.4
	128	31.72	94.4
	130	34.46	97.4
Barium	130	0.101	16.0
	132	0.097	7.43
	134	2.42	51.39
	135	6.59	67.32
	136	7.81	50.02
	137	11.32	38.98
	138	71.66	98.04
Lanthanum	138	0.089	0.597
	139	99.911	99.96
Cerium	136	0.193	16.4
	138	0.250	8.9
	140	88.48	98.5
	142	11.07	87.4
Neodymium	142	27.13	93.00
	143	12.20	83.93
	144	23.87	93.45
	145	8.30	78.60
	146	17.18	95.60
	148	5.72	89.85
	150	5.60	94.76
Samarium	144	3.16	72.13 (101)
	147	15.07	81.63 (199)
	148	11.27	76.01
	149	13.84	71.53
	150	7.47	74.09
	152	26.62	89.90
	154	22.53	92.10
Hafnium	174	0.18	7.85
	176	5.30	48.86
	177	18.47	61.71
	178	27.10	80.91
	179	13.84	46.57
	180	35.11	93.96
Wolfram	180	0.122 (86, 87)	9.0
	182	25.77	94.25
	183	14.24	86.21
	184	30.68	95.72
	186	29.17	97.94
Rhenium	185	37.07	85.38 (10)
	187	62.93	98.22
Mercury	196	0.15 (164)	8.44 (46, 96)
	198	10.1	83.29
	199	17.0	73.09
	200	23.3	91.3
	201	13.2	71.9
	202	29.6	98.3
	204	6.7	92.8
Thallium	203	29.1	86.0
	205	70.9	98.6
Lead	204	1.5	27.0
	206	23.6	81.0
	207	22.6	66.9
	208	52.3	96.5

Total Number of Elements Processed—43
Total Number of Isotopes Processed—177
* No Mass Analysis Performed.
** Mass Analysis in Process.

number of shipments, the number of recipients, and the number of requests awaiting delivery.

TABLE IV

A Summary of Stable Isotopes Produced and Shipped January 1, 1946, to December 31, 1950

	Number
Isotope Samples Completely Processed	828
Individual Elements Processed	43
Individual Isotopes Enriched	177
Shipments Completed	993
Laboratories Receiving Shipments	53
Requests for Isotopes Awaiting Production	54

Isotopes Enriched Only During the Year 1950

The year 1950 has seen the electromagnetic separation of isotopes advance in all of its fields of endeavor. Several elements have been processed in the calutrons for the first time, and others previously run have again been processed to fill special requests or to replenish the inventory. Experimental work has been carried out on determining proper techniques for processing the inert gases as well as the palladium and platinum triads. Calutron facilities have been developed for processing the remaining rare earths as charge materials become available. The chemistry group has made material progress in preparing the rare earth charge material. An investigation is also under way to see if chemical separation of the rare earths must necessarily precede

TABLE V

Elements Whose Isotopes Were Enriched During the Year 1950

Carbon	Lead
Strontium	Neodymium*
Bromine	Indium
Gallium*	Sulphur
Zinc	Hafnium*
Wolfram	Chromium
Samarium*	Calcium
Titanium	Rubidium*
Potassium	Lithium
Iron	Vanadium*

* Separated in the calutron for the first time during 1950.

the isotope separation, or if unit mass separations from mass 136 (Ce) to mass 176 (Lu) could precede chemical separation of the rare earths. Table V lists the elements whose isotopes were enriched during 1950. Figure 4 is a

portion of the periodic chart portrayed in such a way as to illustrate the progress made in enriching stable isotopes. Those elements having only natural radioactive isotopes are not included.

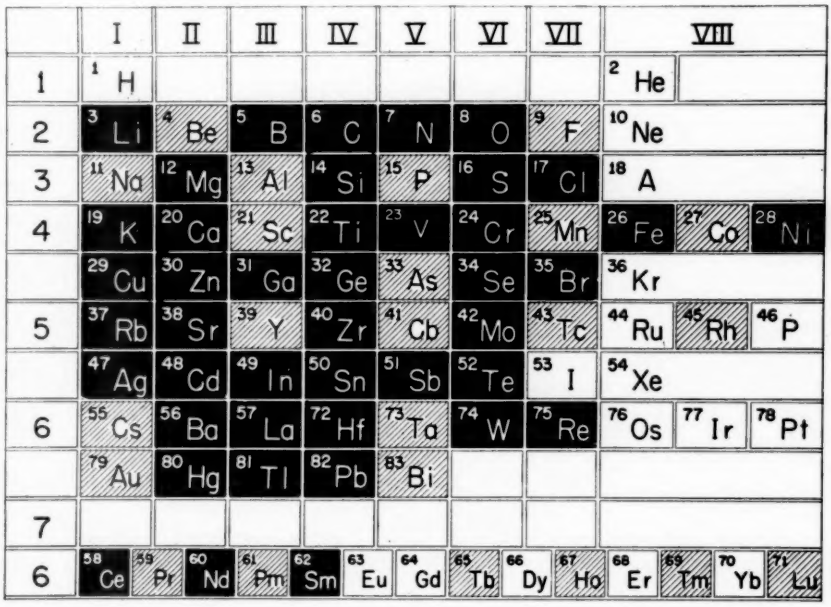

FIG. 4. Isotopes which have been successfully enriched in the calutron from January 1, 1946, to December 31, 1950.

HOW STABLE ISOTOPES ARE USED

What are the research laboratories doing with these separated natural isotopes, most of which are stable? A review of the scientific literature reveals a wide variety of fields in which the separated isotopes have served as valuable research tools (1, 23, 97, 188, 215)

Mass assignments of radioactive isotopes.—Enriched stable isotopes are being used as starting materials in the assignment of masses to artificially produced radioactive isotopes. Also, the accompanying disintegrations are investigated. The tabulation in Table VI summarizes many of these applications of enriched isotopes.

Reactions leading to Fe^{53}, Mn^{57}, and Cr^{55} have been investigated in which separated Cr^{50}, Cr^{54}, and Fe^{57} isotopes were employed. Fe^{53} was prepared from enriched Cr^{50} and the presence of positrons and the Fe^{53} half-life were confirmed. Attempts to produce Mn^{57} by a Cr^{54} (α, p) reaction were unsuccessful, but Mn^{56} from Cr^{53} (α, p) was observed. Similar results were obtained for

TABLE VI

STABLE ISOTOPES EMPLOYED IN CONFIRMATION OF RADIOACTIVE MASSES

Enriched Stable Isotopes Employed	Radioactive Isotopes Produced	Bibliography Reference
Ti^{46}, Ti^{47}, Ti^{49}, Ti^{50}	V^{47}, Sc^{47}, Sc^{48}	111
Ni^{62}, Ni^{64}	Ni^{65}	31
Ni^{64}, Zn^{67}	Cu^{61}, Cu^{67}	118
Cu^{63}	Zn^{63}	58
Cu^{63}, Cu^{65}	Ni^{65}	196
Ge^{70}	Se^{73}	35
Ge^{76}	Ga^{67}, Ge^{69}, Ge^{71}, Ge^{75}	136
Ge^{70}, Se^{74}, Se^{76}	As^{73}, As^{72}, As^{71}	137
Se^{74}, Se^{76}	Kr^{77}, Kr^{79}	210
Se^{74}, Se^{76}	Br^{75}, Br^{77}, Br^{80}	211
Sr^{84}	Y^{84} or Y^{85}, Y^{87}, Zr^{87}	180
Sr^{84}, Sr^{86}, Sr^{87}	Y^{84}, Y^{88}, Zr^{87}	173, 174
Zr^{90}, Mo^{92}	Cb^{90}	117
Zr^{90}, Zr^{91}, Mo^{92}, Mo^{94}, Mo^{98}	Mo^{93}	112
Zr^{90}, Zr^{91}, Zr^{92}, Zr^{96}	Cb^{96}	116, 117
Mo^{92}, Mo^{94}	Ru^{95}, Tc^{95}, Ru^{97}	49
Mo^{92}, Mo^{97}, Mo^{98}, Mo^{100}	Tc^{92}, Tc^{93}, Tc^{100}, Tc^{101}	156
Mo^{94}, Mo^{95}, Mo^{98}	Tc^{94}, Tc^{95}, Tc^{98}	157
Mo^{95}, Mo^{96}, Mo^{97}	Tc^{95}, Tc^{96}, Tc^{97}	158
Mo^{92}, Mo^{94}, Mo^{98}	Tc^{92}, Tc^{93}	115
Mo^{92}, Mo^{94}	Mo^{91}, Mo^{93}	43, 117
Mo^{92}, Mo^{94}, Zr^{90}, Zr^{91}	Mo^{93}	113
Mo^{100}, W^{186}	Nb^{99}, W^{185}, Ta^{185}	40
Ag^{109}	Ag^{110}	67
Cd^{114}, Cd^{116}	Ag^{111}, Ag^{112}	41
Cd^{106}, Cd^{108}, Cd^{110}	Sn^{111}	83
Cd^{106}, Cd^{108}, Cd^{110}	In^{107}, In^{108}, In^{109}, Sn^{108}	125
Cd^{114}, Cd^{116}, Sn^{116}, Sn^{117}, Sn^{118}, Sn^{120}	Sn^{117}	126
Cd^{108}, Cd^{114}	Cd^{109}, Cd^{115}	34
Cd^{114}, Cd^{116}, Sn^{116}, Sn^{117}, Sn^{118}	Sn^{117}	127
Sn^{124}	Te^{125}	57
Sn^{119}, Sn^{120}	In^{118}, In^{119}	42
Sn^{120}, Sn^{122}, Sn^{124}	Sn^{121}, Sn^{123}, Sn^{125}	121
Sn^{116}, Sn^{118}, Sn^{120}, Sn^{122}	Sn^{117}, Sn^{119}	152
Sb^{121}	I^{124}	130
Te^{122}, Te^{124}	Xe^{125}, Xe^{127}	11
Ba^{132}, Ba^{134}, Ba^{135}, Ba^{136}	Ba^{135}	172
W^{183}, W^{183}	Re^{182}, Re^{183}, Re^{186}	47
Re^{185}, Re^{187}	Ir^{187}, Ir^{188}, Ir^{190}	30

the Fe^{57} (n, p) reaction in which no Mn^{57} was found, but Mn^{56} from Fe^{56} was present. The reaction Cr^{54} (d, p) Cr^{55} was unsuccessful as was Fe^{58} (n, α) Cr^{55} (63, 153, 161).

Studies of the disintegrations of radioactive isotopes.—All 10 natural isotopes of tin have been enriched and some of them (Sn^{116}, Sn^{118}, Sn^{120}, Sn^{122}, Sn^{124}) have contributed to the preparation of radioactive isotopes whose radiations have been studied. Artificially produced Sn^{117}, Sn^{119}, Sn^{121}, Sn^{123}, Sn^{125} have all been explored in this way (44, 45, 73, 104, 127, 151). In addition, the probable natural activity of Sn^{124} has been examined, using enriched and impoverished Sn^{124}. From the double beta decay of Sn^{124} a half-life between $3.3 \cdot 10^{10}$ years and $0.9 \cdot 10^{16}$ years was obtained (53). Other studies, however, led to the prediction that the half-life of Sn^{124} is probably greater than 10^{16} years (120).

Disintegration schemes of I^{124} and I^{126} were determined, the radioactive iodine isotopes having been produced by using enriched Sb^{123}, as well as natural antimony, as starting materials. I^{124} decays to Te^{124}, and I^{126} to Xe^{126}. An observed activity was also assigned to I^{123} from these data (154).

Radioactive masses at Y^{87} and Sr^{87} were confirmed by the use of the $Sr^{84}(\alpha, p)Y^{87}$ reaction in which separated Sr^{84} was used. Y^{87} decays by K capture to Sr^{87}. The characteristic radiations of these isotopes were observed and measured (174).

Zr^{97}, produced by $Zr^{96}(n, \gamma)$, and Nb^{97}, from $Mo^{98}(\gamma, p)$ were examined by β-ray spectrometry and coincidence counting; Zr^{97}(17.0 hr.) decays to Nb^{97}(60 sec.) and Nb^{97} undergoes isomeric transition to the Nb^{97}(75 min.) ground state (27).

The decay scheme of Sc^{44} has been studied, the Sc^{44} having been prepared by $K^{41}(\alpha, n)$ in which enriched K^{41} was used (36). The disintegration of Sc^{44} involves an isomeric transition in the parent nucleus, a period of 52 days having been formerly found. Besides the above coincidence studies, the beta disintegration of Sc^{44} was also examined by a magnetic field spectrometer, the isotope again having been prepared from enriched K^{41} (25, 26).

Enriched isotopes of nickel, zinc, selenium, and tellurium were used as tracers in a mass spectrometer investigation of branching in radioactive Cu^{64}, Br^{80}, Br^{82}, and I^{128}, all produced by (n, γ) reactions (168).

Enriched Cd^{108} and Cd^{114} were irradiated in the pile to produce 250-day Cd^{109} and Cd^{115}, the Cd^{115} being isomeric with half-lives of 54 hr. and 42.6 days; the beta and gamma activities associated with these isotopes were also investigated (33).

By using enriched In^{115}, it has been conclusively proven that In^{115} emits a natural beta radiation of 0.63 ± 0.03 M.e.v. energy with a half-life of $6 \pm 2 \times 10^{14}$ years, and that the maximum energy of accompanying gamma radiation consistent in a 1:1 ratio with the beta disintegration rate is of the order of 100 k.e.v. (133)

Enriched Li-6 has been employed in the Li-6(d, p)Li-7 reaction in which the energy released was measured to be 5.006 ± 0.014 k.e.v. (189).

Photoneutrons from enriched isotopes.—The thresholds for photoneutron reactions were determined on enriched Zn^{70} in which x-rays from the betatron were employed, the observed threshold being 9.20 ± 0.20 M.e.v. as compared with an empirical binding energy of 10.1 and 10.4 M.e.v. (70).

The neutrons from deuteron bombardment of enriched Li^6 have been measured for deuterons between 250 and 2200 k.e.v., using a Van de Graaf generator (202). These neutrons come from the two reactions: $Li^6+H^2 \rightarrow (Be^8) \rightarrow Be^7+n+3.3$ M.e.v., and $Li^6+H^2 \rightarrow (Be^8) \rightarrow He^4+He^3+n+1.7$ M.e.v.

From the plotted excitation curves for Li^6 and Li^7, it was seen that at a given energy the relative number of neutrons from Li^7 is several times greater than from Li^6. Li^7 has a resonance at 1,020 k.e.v. Excitation curves for the protons from competing reactions have also been worked out. These reactions are: $Li^6+H^2 \rightarrow (Be^8) \rightarrow Li^7+H^1+5.0$ M.e.v., $Li^6+H^2 \rightarrow (Be^8) \rightarrow Li^7+H^1+4.5$ M.e.v., and $Li^6+H^2 \rightarrow (Be^8) \rightarrow He^4+He^4+22$ M.e.v.

An interpretation of results by other experimenters, when 0.90 M.e.v. deuterons were used on enriched Li^6 in the above two reactions, indicated that the neutron yield, as measured by proton recoils in photographic emulsions, of the first reaction shown, $Li^6(d, n)Be^7$, is about twice that of the second reaction, $Li^6(d, n\alpha)He^3$.

Wilson cloud chamber measurements in which 595 k.e.v. deuterons from a Van de Graaf were used (201) on Li^6 showed that fewer than one-half of the neutrons came from the reaction $Li^6+H^2 \rightarrow Be^7+n+3.30$ M.e.v. as compared to the reaction $Li^6+H^2 \rightarrow H^4+He^3+n+1.68$ M.e.v.

This does not agree with results which indicated that about two-thirds of the neutrons came from the first reaction (128). It was proposed that either the angular distributions of the neutrons from the two reactions were not the same or that the relative yields of the reactions changed with bombarding energy (201).

Enriched Li^7 targets, bombarded with 1.1 M.e.v. deuterons produced neutrons by these reactions: $Li^7+H^2 \rightarrow H^4+He^5$, $He^5 \rightarrow He^4+n$, and $Li^7+H^2 \rightarrow Be^8+n$. There are two groups of neutrons from the latter reaction at 1.36 and 4.9 M.e.v. and give levels in Be^8 at 14.7 and 11.1 M.e.v. (204).

Isotopic Mg^{25} was used for investigating the neutron spectrum from the reaction Mg^{25} (d, n) Al^{26} by using deuterons of 1.47 M.e.v. Nuclear energy levels in Al^{26} were located at 2.00, 3.63, and 5.13 M.e.v. from the four groups of neutrons which appeared. The Q value for the formation of Al^{26} in the ground state is 5.58 M.e.v. Bombardment of Mg^{26} by deuterons gave rise to eight groups of neutrons corresponding to energy levels in Al^{27} at 0.88, 1.92, 2.75, 3.65, 4.33, 5.32, and 5.81 M.e.v. The Q value for the formation of Al^{27} in the ground state is 5.68 M.e.v. $Mg^{24}(d, n)Al^{25}$ made no appreciable contribution to the observed spectra of $Mg^{25}(d, n)Al^{26}$ or $Mg^{26}(d, n)Al^{27}$(7, 66, 194, 195).

Enriched Si^{28}, Si^{29} and Si^{30} have been bombarded with 3.8 M.e.v. deuterons from a cyclotron in which the following reactions occurred: $Si^{28}(d, p)Si^{29}$, $Si^{29}(d, p)Si^{30}$, and $Si^{30}(d, p)Si^{31}$. The ground state transition for $Si^{28}(d, p)Si^{29}$ was found to be 6.18 M.e.v. and that for $Si^{29}(d, p)Si^{30}$ to be 8.36 M.e.v. Seven proton groups corresponding to excited states in Si^{29} were observed, three groups leading to excited states in Si^{30}, and five associated with Si^{30} $(d, p)Si^{31}$. A sixth proton group was in doubt (159).

Neutron absorption cross section measurements.—Enriched stable isotopes of high chemical purity are being utilized for the determination of their isotopic cross sections (20, 166, 167). Using the pile oscillator at Oak Ridge National Laboratory (ORNL), some of the values for thermal neutron absorption cross sections first reported were as follows: Ag^{107}, 30.1 b; Ag^{109}, 83.7 b; Ni^{58}, 4.3 b; Ni^{60}, 2.7 b; Fe^{54}, 3.1 b; Fe^{56}, 3.1 b; and Fe^{57}, 0.5 b. (1 barn = 10^{-24} sq. cm.). The value for gold, 95 b, was used for comparison (167). Recent results for thermal neutron capture cross sections of almost 50 different isotopes are summarized in Table VII.

Cross section measurements, other than neutrons.—Enriched Mo^{94}, as well as natural molybdenum as the element, were bombarded with protons and deuterons. The variation of isotopic percentage in the targets made it possible to set up a system of equations, each related to a different activity, with the cross sections as unknowns. When the bombarding beam was properly monitored, these simultaneous equations could be solved to give the relative cross sections, if the details of the decay scheme of the radioactive products were known. For 5 M.e.v. protons: $Mo^{94}(p, \gamma):Mo^{95}(p,n):Mo^{95}(p, \gamma):Mo^{96}(p, n) = 1:260:40:400$. For 10 M.e.v. deuterons: $Mo^{94}(d, n):Mo^{95}(d, 2n)$ $Mo^{95}(d, n):Mo^{96}(d, 2n) = 1:13:17:2.5$ (114).

The compound nucleus Zn^{64} was formed in two reactions, alpha bombardment of Ni^{60} and proton bombardment of Cu^{63}. The ratios of the cross sections for $Ni^{60}(\alpha, n):Ni^{60}(\alpha, 2n):Ni^{60}(\alpha, pn)$ agreed with the ratios for $Cu^{63}(p, n):Cu^{63}(p, 2n):Cu^{63}(p, pn)$ giving support to the theory of the compound nucleus (62).

The cross sections of the $Li^6(d, \alpha)\alpha$ and $Li^6(d, p)Li^7$, $^*Li^7$ reactions were measured up to deuteron energies of 1,600 k.e.v. (200). Evidence was obtained for a resonance level of 347 k.e.v. in Be^8, and the complexity of the angular distribution was found to increase with the energy of bombardment.

Coherent neutron scattering cross sections.—The coherent scattering cross sections of Ni^{58}, Ni^{60}, and Ni^{62} were measured with the crystal spectrometer to see if the difference between the total and coherent scattering cross sections was due to the isotope effect. Enriched stable isotopes were employed in the form of the oxide (108).

The neutron diffraction patterns showed, in addition to the nuclear peaks which varied from isotope to isotope, antiferromagnetic reflections which were identical in all samples within experimental error. The scattering cross sections were found to be: Ni^{58}, 27.6 b; Ni^{60}, 0.97 b; Ni^{62}, 9.1 b; and for ordinary Ni, 13.3 b. Differences among the isotopes in their scattering properties, from the potential scattering value for Ni of about 4.4 b, were thought to indicate a strong contribution for resonance effects (109).

Coherent scattering cross sections and nuclear resonances were investigated with enriched Te^{124}. A strong resonance had been observed at 2.2 e.v. on normal tellurium and investigations were made to see if it was an isotope effect (74).

Employing enriched isotopes of Fe^{54}, Fe^{56}, and Fe^{57}, as well as ordinary

TABLE VII

THERMAL NEUTRON CAPTURE CROSS SECTIONS OF ISOTOPES (166)

Isotope		Capture Cross Sections*		
		Isotopic	Error (%)	Atomic
Magnesium	24	0.033 b	30	0.026 b
	25	0.27	30	0.027
	26	0.06	100	0.006
Silicon	28	0.08	30	0.075
	29	0.27	30	0.012
	30	0.41	100	0.013
Titanium	46	0.57	30	0.05
	47	1.62	20	0.13
	48	7.98	8	5.86
	49	1.80	25	0.10
	50	0 (±0.2)		0
Chromium	50	16.3	8	0.73
	52	0.73	8	0.61
	53	17.5	8	1.65
	54	0 (±0.3)		0
Nickel	58	4.23	8	2.87
	60	2.70	8	0.71
	61	1.8	75	0.54
	62	15	20	0.02
Copper	63	4.29	8	2.96
	65	2.11	8	0.65
Germanium	70	3.3	8	0.69
	72	0.94	10	0.26
	73	13.7	8	1.08
	74	0.60	10	0.22
	76	0.35	20	0.02
Selenium	74	44	20	0.38
	76	82	10	7.39
	77	40	10	3.01
Zirconium	90	0.1†	—	0.06
	91	1.52	10	0.17
	92	0.25†	—	0.04
	94	0.08 (0.06)†	—	0.01
	96	0.1 (0.045)†	—	0

TABLE VII (*Continued*)

Isotope		Capture Cross Sections*		
		Isotopic	Error (%)	Atomic
Molybdenum	95	13.4	8	2.11
	96	1.2	50	0.20
	97	2.1	30	0.20
	98	0.38	100	0.09
	100	0.5	100	0.05
Silver	107	30.0	8	15.6
	109	83.7	8	40.3
Tellurium	120	68	100	0.07
	122	2.7	35	0.07
	123	390	8	3.49
	124	6.5	20	0.30
	125	1.5	10	0.10
	126	0.77	25	0.14
	128	0.3	100	0.09
	130	0.5	50	0.18

* The values were determined with the ORNL pile oscillator by comparison with gold, for which the value of 95 b for neutrons of 0.025 e.v. was used. The errors shown in the table are estimates which include the instrumental error and the adequacy of the sample sizes, but which also assume that the assays of the isotopes are without error. Because in general only one enriched sample was available for an isotope, the limiting accuracy of the measurements is thought to be about 8 per cent. The atomic values are found by multiplying the isotopic values with the relative natural abundances.

† Hf, and perhaps B also, make the Zr values uncertain except for Zr^{91}. The values in parentheses are activation values by S. Reynolds and G. Leddicotte of ORNL using the same samples.

Fe, the coherent scattering cross sections were determined by neutron diffraction. The coherent scattering cross sections in barns were found to be 12.6 b for Fe^{56}, 2.2 b for Fe^{54}, 0.64 b for Fe^{57}, and 11.5 b for Fe as the element (107).

Neutron detection.—Li^6 isotopes were used in photographic plates for measuring the energy of fast neutrons by the nuclear reaction $Li^6(n, \alpha)H^3$. In commercial lithium loaded plates, the disintegrations are masked by a high background of proton tracks (90). It is reported that this analysis method permits the measurement of monoenergetic neutrons from thermal to 1.3 M.e.v. to a precision of at least ± 0.1 M.e.v. This is particularly suited to the measurement of the energy distribution of fast neutrons in a material medium because collimation of the neutrons is not necessary and perturbations introduced by the detector are minimized (91, 92, 171).

Isotope shift, hyperfine structure, and nuclear spin.—Hyperfine structure, nuclear spins, and nuclear magnetic moments have been investigated with several enriched isotopes. The stability of the isobaric pair In^{115}/Sn^{115} was investigated by using enriched isotopes. The nuclear spin of Sn^{115} was found to be 1/2, and since it had been known that the spin of In^{115} is 9/2, it can be concluded that the transition from Sn^{115} to In^{115} is highly forbidden on the basis of a spin change of four (68).

With the determination that the spin of Te^{123} is 1/2, the three known pairs of neighboring isobars among the stable isotopes and their spins are:

$$Cd_{1/2}{}^{113}—In_{9/2}{}^{113}$$
$$In_{9/2}{}^{115}—Sn_{1/2}{}^{115}$$
$$Sb_{7/2}{}^{123}—Te_{1/2}{}^{123}.$$

Fe^{57} was inspected for hyperfine structure. No structure was found between 4000 Å to 6800 Å and between 2400 Å and 6000 Å. As is true with similar nuclei whose mass is odd but whose nuclear charge is even, Fe^{57} has no measurable magnetic moment (24, 69).

Te^{125} has been observed to have hyperfine structure between 4000Å to 6000 Å; it was concluded that the spin for Te^{125} is 1/2 (55). By using enriched Te^{123}, the nuclear spin was found to be 1/2 and an isotope shift is evident in several lines of the tellurium spectrum (124).

With the aid of enriched Te^{123}, Te^{125}, and W^{183}, the hyperfine structures in their optical spectra have been observed and the nuclear spins for these isotopes found to be 1/2 (56).

Interference spectrograms of enriched Zr^{91} indicated that its nuclear spin is 5/2 (15).

Spectroscopic studies of the hyperfine structure and isotope shift using enriched Ba^{137} and Ba^{135} showed that both lines have a spin of 3/2 and that the splittings from Ba^{137} are 12 per cent greater than those from Ba^{135}; also, a small isotope shift was found in which the even isotopes are displaced with respect to the odd. Isotope shift and spectroscopic hyperfine structure studies with enriched barium isotopes have confirmed a nuclear spin of 3/2 for Ba^{135} and Ba^{137}; the lines of the even barium isotopes showed no hyperfine structure (12, 13).

The isotope shift and the Pb^{207} hyperfine structure have been measured using enriched lead isotopes; it was concluded that these isotope shifts indicate decreasing nuclear stability in progressing from 204 to 208 (129, 197). Pb^{204} and Pb^{207} in an enriched form were used in studying the isotope shift in Pb^{II} (61).

Ni^{61} in the enriched form did not show clear hyperfine structure splitting but certain lines showed definite broadening greater than that caused by the Doppler effect. The resolution was insufficient to determine the spin but the upper limit of the magnetic moment appeared to be of the order of 0.25 nuclear magneton (103). Enriched Mo^{95} and Mo^{97} showed that the nuclear spin of these isotopes is not 1/2 (14).

Spectrum shifts as large as a wave number between the U^{235} and U^{238} spectra, the shifts usually being toward the violet for the light isotope, have been investigated with enriched isotopes of uranium (140, 143). Preliminary spectroscopic studies on enhanced U^{235} point to a nuclear spin of 5/2 and supply strong evidence for the existence of a nuclear electric quadrupole moment, arising from asymmetry of the nuclear charge distribution (190, 191). Numerous samples containing enriched uranium isotopes U^{233}, U^{234}, U^{235}, and U^{238} have all been spectrographically studied for isotope shifts.

The isotope shifts in a radioactive sample of 13 per cent Th^{230} and 87 per cent Th^{232} have been measured (144). Shift data on the uranium 4244 Å line for these four isotopes are given in Table VIII.

TABLE VIII

URANIUM ISOTOPE SHIFTS IN LINE 4244 Å

Isotope	λ	Δλ
238	4244.373	0.000
235	4244.122	0.251±0.002
234	4244.075	0.298±0.003
233	4243.977	0.396±0.005

Enriched Hg^{202} was examined as a possible source for monochromatic light and Fabry-Perot interferograms show that Hg^{202} in 98.06 per cent isotopic purity provides a reproducible wavelength at the 5461 Å line (142). Hg^{202} enhanced to greater than 98 per cent isotopic purity has been studied at high resolution by employing a 1,500 megacycle source (65). Resolutions greater than 1,000,000 have been obtained with no deleterious effects from isotopic impurities in the Hg^{202} spectra. Theoretical considerations have been proposed which show that the reproducibility of the wavelength of the green line of mercury in such a Hg^{202} source should be affected by considerably less than one part in 50,000,000 by the satellite structure due to other isotopes. Figure 5 shows the Fabry-Perot interference pattern for enriched Hg^{202} compared with the pattern for normal Hg.

Hg^{198} is a natural stable isotope and can be enriched in the calutron, but it is also successfully produced in the pile from gold. The advantages of Hg^{198} as a primary standard of wavelength have been considered thoroughly and the bibliography at the close of this chapter covers the subject quite fully (21, 64, 88, 102, 141, 145 to 150, 160, 205 to 208).

Hyperfine studies on the only naturally occurring odd mass isotope of calcium have been made with enriched Ca^{43} (65).

Enriched S^{33} made it possible to investigate the hyperfine structure of that isotope and to determine its nuclear magnetic moment as 0.632±0.010 nuclear magneton (50).

Isotopic displacements of spectrum lines have been observed in lithium,

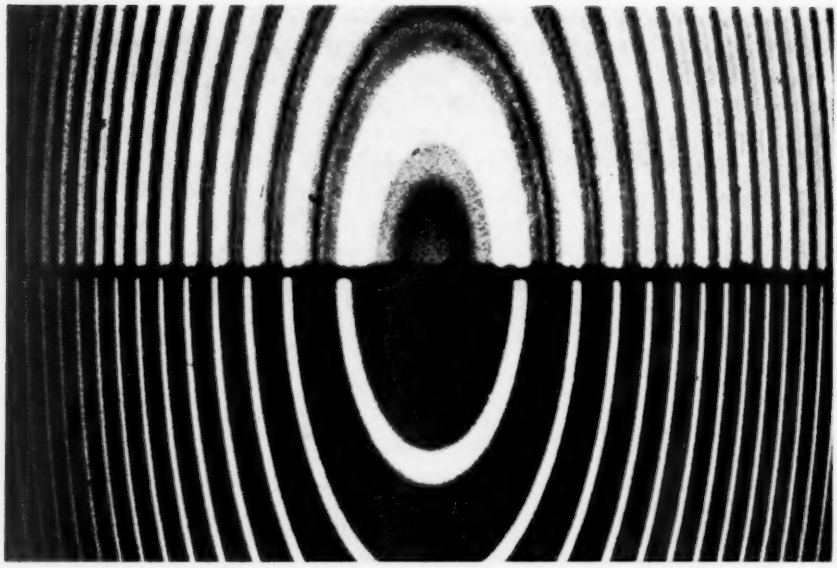

FIG. 5. Interferometric comparison of 5461 Å lines in enhanced Hg^{202} (98.30 per cent) and in natural mercury. Complex pattern of natural mercury due to hyperfine structure of odd mass isotopes.

samarium, thorium, and uranium. McNally (144a) has reported that separated isotopes of Li^6 and Li^7 give positive proof that the shift in the resonance line is identical with the fine structure separation as first suggested by Schuler & Wurm (178).

The extreme mass isotopes of samarium, Sm^{144} and Sm^{154}, have been studied spectrographically using samples which have been enhanced to 75 per cent and 92 per cent, respectively (185). Isotope shifts as large as 0.4 Å were measured. The isotope shifts are shown in Figure 6.

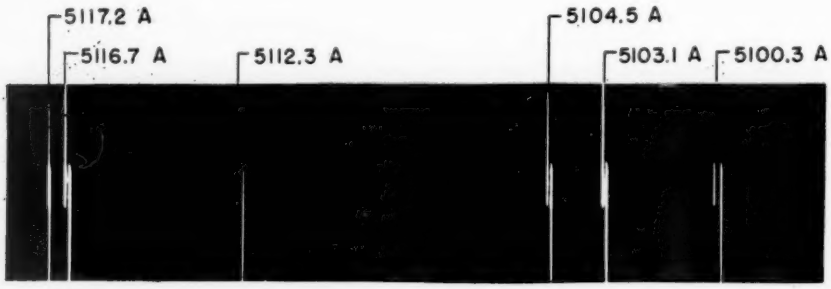

FIG. 6. Spectrum shifts in enhanced samarium samples. Top spectrum is Sm^{144}. Middle spectrum is the superimposed spectra. Bottom spectrum is Sm^{154}.

The hyperfine structure and nuclear spin of Kr^{83} and Ne^{21} were studied at Copenhagen, Denmark, where they used isotopes enriched by their mass spectrograph. Very pure Kr^{82}, Kr^{83}, and Kr^{84} were prepared. A spin of 9/2 and the existence of a quadrupole moment for Kr^{83} were definitely confirmed. With Ne^{21} the magnetic moment was found to be negative and the spin to be 3/2 or perhaps greater (105).

In these same laboratories, the xenon isotopes 129, 130, 131, 132, 134, and 136 were prepared. For Xe^{129} a spin of 1/2 was determined, for Xe^{131} a spin of 3/2. Also, for Xe^{131} the existence of a quadrupole moment of the same size as for Kr^{83}, but of opposite sign, was determined (106).

Nuclear energy levels.—By using enriched isotopes, nuclear energy levels have been determined for a number of isotopes of different elements. Targets of separated K^{39} and K^{41} were subjected to (*d*, *p*) reactions, the energy distribution of the emitted protons was measured, the mass differences between K^{40}/K^{39} and K^{42}/K^{41} found, and excited states of K^{40} and K^{42} were located (175).

Energy levels in lead, bismuth and thallium have been investigated using enriched isotopes of lead, Pb^{206}, Pb^{207}, and Pb^{208}, as well as bismuth and thallium elements (2, 71). Selenium enriched in Se^{74} was used to produce radioactive Se^{75}; the electron energies were then determined, as well as the gamma-energies (32). Energy levels of Si^{28} had been studied by means of proton bombardment of Al^{27} but, when analysis of the results proved ambiguous, separated Mg^{24} was used as a target for alphas; a Q-value of -1.62 M.e.v. for the reaction Mg^{24} (α, *p*) Al^{27} was found (89).

Separated Ag^{107} and Ag^{109} were excited to their metastable states by x-rays; the thresholds for x-ray excitation, the activation levels, the over-all cross sections, and the activities of the excited products were all investigated (209). When a thick target of isotopic Mg^{26} was irradiated by deuterons, eight groups of neutrons were seen corresponding to energy levels in Al^{27}; the Q-value for the ground state is 5.68 M.e.v. (193).

Isomerism.—Enriched tellurium isotopes, masses 122, 124, 125, 126, 128, and 130, have been employed to produce the tellurium isomers by neutron irradiation. From the internal conversion electron spectra of those isotopes it has been shown that each odd mass number isotope from 121 to 131 exists in a long-lived isomeric state, that a spin of 1/2 exists for the long-lived isomeric state, that the spins of the ground states of Te^{127}, Te^{129}, Te^{131} appear to be 3/2, and the spin of Te^{123} to be one-half (82).

Isomerism in Pb^{204} has been investigated because it is the only even-even nucleus for which a fairly long metastable state is known. Enriched Pb^{204} was used to produce 12-hr. Bi^{204} by the (*d*, 2*n*) reaction from which Pb^{204} was obtained. From γ-ray coincidence studies, it was found that the isomeric transition takes place in two steps (192).

The question of isomerism in Ca^{49} was studied with the Ca^{49} obtained by neutron irradiation of Ca^{48}. Although periods of 30 min and 2.5 hr. had been previously assigned to Ca^{49}, two activities of 8.5 min. and 1 hr. half-life were

found. The 8.5-min. activity was assigned to Ca^{49} and 1-hr. activity to Sc^{49}, the daughter of the 8.5 min. Ca^{49}. The assignment of the 8.5-min. activity was checked by bombarding ordinary calcium as well as enriched Ca^{46} (37).

Enriched stable isotopes Cd^{112}, Cd^{113}, Cd^{114}, and Cd^{116} were employed to assign a 5.1-year activity to an isomer of Cd^{113}. Instead of decaying to the ground state by the emission of γ-rays, β-rays of 0.5 M.e.v. are given off to form In^{113}. The previously assigned 2.3-min. activity to Cd^{113} could not be explained. X-rays were also observed in the decaying of Cd^{113}, but it is not known if they are those of cadmium or of indium (28). The isomerism of Xe^{131} was investigated in which the xenon isotope was separated electromagnetically at Nobel Institute (19).

Superconductivity.—The enriched isotopes of mercury and tin have been used in studies on superconductivity (134, 169, 170). It was also concluded that the product $M^{0.5}T_c = \text{constant}$, where M is the average mass and T_c is the transition temperature for the various mercury isotopes (182, 183). Detailed theories of superconductivity favor the value of 0.5 as the exponent of M (59). However, there is some belief that $M^{0.378}T_c = \text{constant}$ fits the available experimental data better (75).

Comparing natural tin of mass 118.7 with enriched tin^{124} of average mass 123.1, it was seen that an increase in mass shifted the transition temperature to lower temperatures just as was found with various mercury masses; the shift in temperature with tin is 0.012° K. per mass unit and with mercury 0.007° K. per mass unit (8, 9, 75, 135).

Disintegration of K^{40}.—K^{40}, a naturally occurring radioisotope, has been sucessfully enriched in the calutron. This product has then been used in studies involving the beta spectrum of K^{40} and the geochemical significance of its decay. Some of the latest reports produced a Kurie plot which was curved concave towards the energy axis but yielded a straight line down to about 500 k.e.v., the endpoint being at $1{,}325 \pm 20$ k.e.v. (52). Observations by others had shown the Kurie plot to be linear from 500 k.e.v. to the endpoint at 1.38 ± 0.03 M.e.v. (5); and an endpoint at 1.36 ± 0.005 M.e.v., with the Kurie plot concave to the energy axis above 700 (18).

It was concluded that the β-ray spectrum of K^{40} may be regarded as agreeing with the theory of Marshak (4, 132), although earlier results with less enriched K^{40} had indicated a shape of the allowed type of spectrum which was in contradiction to the theory of forbidden beta decay and the predictions of Marshak (3).

Other experiments with enriched K^{40} were on the gamma spectrum with the scintillation counter (17). It was observed that 88 per cent of the K^{40} decays were by betas and 12 per cent by electron capture, and that the γ-rays were associated with electron capture decay (177). Other reports gave a value of 7.9 ± 0.3 for the ratio of beta emission to K capture; another stated that the ratio of disintegration constants for electron capture to beta emission was less than 20 per cent (52, 76, 176). A half-life value for K^{40} was placed at $12.7 \pm 0.5 \times 10^8$ years (177). Other reports on K^{40} have been in-

cluded in the bibliography and provide a rather complete survey of this situation (22, 48, 54, 184, 198, 212, 213).

Disintegration of Be^{10}.—Be^{10} was produced in the pile by the reaction Be^{9} $(n, \gamma)Be^{10}$. This Be^{10} was then enriched 1,200-fold in the calutron to an isotopic abundance of 0.3 per cent Be^{10} (99). Various investigations were made on this sample of Be^{10}, and all investigators agreed that, with the correction by the D_2 factor of Marshak (131), the experimentally observed Be^{10} spectrum and the theoretically predicted spectrum are in such good agreement that it provides a good test of the present theory of β decay (6, 16, 51, 52, 84, 85). The maximum energy of the β-rays was found to be 0.545 ± 0.010 M.e.v. (16), 560 ± 5 k.e.v. (11, 84), and 555 ± 5 k.e.v. (51). Other references on Be^{10} and beta disintegration are included in the bibliography (60, 139, 165, 212, 213, 214).

In summary, electromagnetically enriched K^{40} and Be^{10} assisted in various ways to establish the β-ray spectra which had been theoretically investigated and predicted by Marshak (131, 132). Those who used enriched Be^{10} all found that the Be^{10} spectrum agreed well with Marshak's D_2 spectrum.

Quoting C. S. Wu (213),

> The experimental observation of the three unique forbidden spectra of Y^{91}, Be^{10} and K^{40} as theoretically predicted is a triumphant test for the theory of forbidden beta-decay . . . . The fruitful year which has just passed was made possible only through the concerted efforts of all those who are interested in this field.

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CHEMICAL SEPARATION OF STABLE ISOTOPES

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In the last several years many methods have been developed and used for the separation of stable isotopes. The electromagnetic process has demonstrated its versatility by separating research quantities of the isotopes of almost all of the elements.[1] The highly successful separation of uranium isotopes by gaseous diffusion is now routine. Commercial use is being made of Dr. Urey's chemical exchange process in the production of C^{13} and N^{15}.[2] Other isotope separations are being made in routine fashion by thermal diffusion and distillation as well as chemical exchange to produce usable quantities of O^{18}, S^{34}, S^{36}, and isotopes of the rare gases. In fact it is now generally believed that the isotopes of any element can be separated in quantity if the need be great enough to meet the costs. Usually, where large quantities are desired and cost must be considered, attention is directed toward chemical means of separation. The chemical exchange methods are usually considered to be economically superior to most other methods for all light elements except hydrogen. At least, for those light elements for which a chemical exchange system has been devised, it has proved to be less costly than the other available methods. This, of course, does not mean that isotope separation by any method is anything but an extremely difficult production undertaking. Many new methods have been proposed and improvements have been made on the older processes, but separated stable isotopes continue to be costly.

The preceding statements are in reference to the actual production of usable quantities of substances with sizably altered isotopic abundance. This is in contrast to small changes in isotopic ratio achieved in minute quantities of materials in a laboratory experiment. It seems desirable to distinguish between a practical production process capable of commercial operation and a "laboratory demonstration" of isotope separation which may be no more than the observation that a slight enrichment occurs in a single laboratory operation. In reviewing the separation of isotopes by chemical means, it would seem at first that the subject matter should be confined to those procedures which have been used successfully in the past or show great promise of successful demonstration in the future. However, a great many isotope separation schemes and improvements which appear to be of doubtful or borderline value as known today might be transformed into highly desirable efficient processes by some small change conceived of later. Consequently, this paper will cover some material on isotope separation which may be of marginal utility on a commercial scale yet forms a part of the whole picture of the status of this problem.

[1] See the chapter on "Electromagnetic Separation of Stable Isotopes" by C. P. Keim.

[2] See Organic Chemical Sales Divisions, Eastman Kodak Co., Rochester 4, N. Y.

An isotope separation process or system must meet several specifications if successful production is to result. These various requirements help to define a group of related fields of inquiry wherein progress in research and development is of substantial importance to the over-all problem of separating stable isotopes. This becomes evident if the important features of a chemical exchange process are examined, with detailed study of progress in the various lines of study thus defined. The various criteria of a successful chemical exchange process might be expressed as follows, using specific features of the very well known N^{15} process (1) for illustration:

(*a*) The element should be distributed between two phases:

$$NH_3 \text{ (gas phase)} \cdots NH_4^+ \text{ (liquid phase)}.$$

(*b*) Rapid isotopic exchange must take place between the chemical forms in the two phases

$$N^{15}H_3 + N^{14}H_4^+ \rightleftarrows N^{14}H_3 + N^{15}H_4^+.$$

(*c*) The equilibrium constant of the isotopic exchange reaction must be other than unity

$$k = \frac{[N^{14}H_3][N^{15}H_4^+]}{[N^{15}H_3][N^{14}H_4^+]} = 1.035 \text{ at } 298°K.$$

(*d*) Means for achieving total reflux at the top or bottom of the plant must be provided:[3]

reflux of NH_4^+

$$NH_4^+ + NaOH \rightarrow NH_3 \uparrow + Na^+ + H_2O,$$

reflux of NH_3

$$NH_3 + HNO_3 \rightarrow NH_4^+ + NO_3^-.$$

The first of these criteria which concerns the distribution between two phases is obviously important in facilitating countercurrent movement of the two chemical forms of the element. A rigid stipulation that it must be two phases has been avoided, since two methods of achieving countercurrent flow in a single phase have been proposed. Bernstein & Taylor (2) were able to obtain enrichment of carbon-13 by using the thermal diffusion principle to obtain countercurrent flow in the system

$$C^{13}O + C^{12}O_2 \rightleftarrows C^{12}O + C^{13}O_2.$$

Using a cooled cylindrical column with an axial heated element, the desired convective flows were obtained: the CO_2 downward and the CO upward. The isotopic exchange reaction taking place throughout the tube then concentrated the C^{13} in the CO_2 and the C^{12} in the CO. The reflux requirement stated above was met by providing a converter at one end of the column which reduced CO_2 to CO. At the other end of the column a continuous sweep of CO_2 provided essentially an infinite reservoir. After comparison of their results with separations achieved by other methods the authors con-

[3] Reflux at both top and bottom must be provided if efficient usage is to be made of feed material.

clude that the power requirements would be much greater than the usual two phase countercurrent exchange process although the method is comparable economically with straight thermal diffusion. Nevertheless it is certainly possible that separation problems may arise for which this scheme offers the only possible solution. Application to liquid systems may be possible if they possess rather specialized properties. It seems generally inapplicable to aqueous systems although small enrichments of zinc isotopes were obtained by Korshing & Wirtz (3) using straight thermal diffusion on water solutions. However, an alternate technique is available for causing countercurrent flow of two different solutes in aqueous systems. Martin (4) has proposed the use of the principle of countercurrent electromigration for

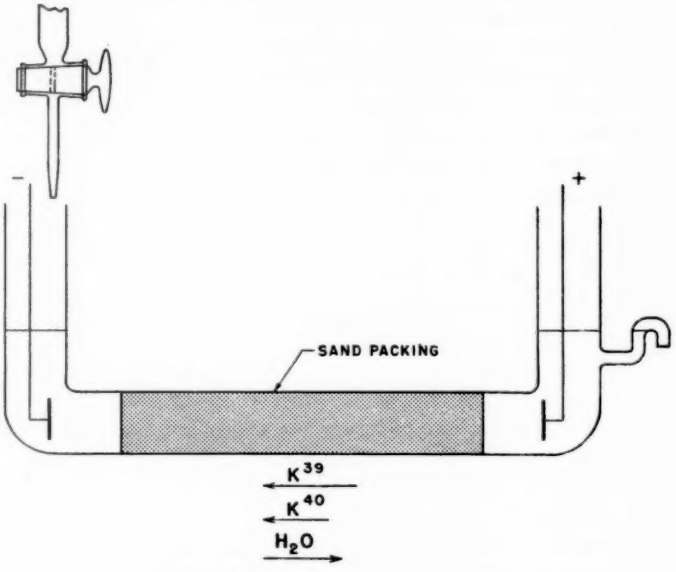

FIG. 1. Electromigration apparatus.

achieving the desired movement of two solute species capable of isotopic exchange. This principle was independently proposed by Clark (14) during the course of the isotope separation studies sponsored by the Atomic Energy Commission. For a clearer understanding of the method it will be helpful to review briefly the countercurrent electromigration studies of Brewer, Madorsky and others (5). The enrichment of the potassium isotopes by these workers serves as a good example. Figure 1 illustrates a few of the essential features of the apparatus which consists of two electrode compartments separated by a horizontal section packed with fine sand. The rate of migration of the potassium ions is almost exactly counterbalanced by the flow of water in the opposite direction. The lighter, faster-moving isotope is able to make headway against the stream and the heavier, slower isotope is washed back by the stream. The result is a buildup of light isotope in the cathode compart-

ment. The separation factor, which is related to the ratio of the isotopic masses, suffers of course from the diminishing effect of the added weight of the water of hydration on the ions. However, a greater disadvantage may be the high power consumption. This can be minimized by using essentially neutral solutions to eliminate any large portion of current being carried by hydrogen or hydroxyl ions. Since this work demonstrates that separation of isotopes can be obtained by such countercurrent electromigration, it becomes apparent that countercurrent flow of two different ionic species should be relatively easy to achieve. If one of these solutes be a neutral molecule in isotopic equilibrium with an ion such as we might have in the exchange

$$\overset{*}{M}^{+} + MX \rightleftarrows M^{+} + \overset{*}{M}X$$

then it appears that the desired flows should be even more probable of attainment. In this type of single phase system, as well as in the single phase gaseous system of Bernstein & Taylor, one obvious advantage over the conventional two-phase system is the close proximity of the species undergoing isotopic exchange. The problems of causing intimate contact of phases and migration across an interface are eliminated and the exchange reaction can take place throughout the entire system. However, the power required to move the reacting substances may well be of such magnitude as to make the method of borderline utility. A final answer on this must await studies on the application to particularly favorable exchange reactions.

Interesting applications of electromigration to lithium and potassium fused salt systems has been made by Klemm, Hinterberger & Hoernes (6). Sizable isotopic enrichments have been made, such as a change of the Li^7/Li^6 ratio from 12.3 to 44 in 130 mg. of LiCl in a small 15 cm. tube.

Returning now to the first criterion for a successful chemical exchange process concerning the preference for two immiscible phases, the various possibilities might be listed as follows: (*a*) gas-liquid; (*b*) liquid-liquid; (*c*) gas-solid; (*d*) liquid-solid.

Almost all of the reported successful processes have consisted of a gas-liquid system, and this type appears to be superior to all others. Examples of these are shown in Table I.

TABLE I

Gas Phase	Liquid Phase	Product	Reference
HCN	CN^- aqueous	C^{13}	7, 8
CO_2	HCO_3^- aqueous	C^{13}	9
NH_3	NH_4^+ aqueous	N^{15}	1
SO_2	HSO_3^- aqueous	S^{34}	10, 11

The efficiency with which countercurrent streams of gas and liquid can be contacted in ordinary distillation type equipment is unquestionably responsible for a large measure of this success.

There appears to be no reason why a liquid-liquid system should not be

satisfactory, yet only one example has appeared: the enrichment of Li^6 by exchange between lithium amalgam and an organic solution of a lithium salt (12). It is true that the greater height equivalent of a theoretical plate to be expected in a liquid-liquid system in contrast to a gas-liquid system is a definite disadvantage in an isotope separation process. This arises from the fact that the large over-all separations to be obtained with such small single-stage factors place a premium on low holdup and high throughput. However, large variation in height equivalent of theoretical plate with solvent characteristics is known to occur, and suitable solvents to minimize this effect might be found for any single case. Also the continuing advances made in liquid-liquid contacting equipment provide some additional hope for this type of system.

Systems involving a solid phase suffer from the disadvantage that it is difficult to achieve countercurrent flow. One novel means of obtaining this in a fractionation process has been demonstrated by Reid (13). The method uses the unidirectional motion of a series of hot and cold regions along an extended passage which contains the mixture to be fractionated. The material is frozen down to a cold spot, but the advancing hot zone vaporizes some of the material. Part of this condenses in the same cold zone while part of it is carried back to the next advancing cold zone. Thus any isotopic difference in vaporization, diffusion, or condensation results in the advance of the condensed phase with continuous concentration of one component against a countercurrent flow of gas being depleted. Of the many possible designs of apparatus embodying this principle, Reid chose a rotating helical coil mounted on a horizontal axis with heat supplied to each upper portion of turn and cold to each lower portion of turn. In experiments with water, Reid reports a 7 per cent enrichment of O^{18} in 25 per cent of the charge after eight minutes of operation in a five-turn coil.

The best known enrichments in liquid-solid systems are those reported by Taylor & Urey using zeolite for the separation of the isotopes of potassium and lithium (15). See also Glueckauf on the use of ion-exchange resins (28).

The second criterion of a successful chemical exchange process concerns the need for rapid isotopic exchange between the chemical forms in the two phases. It appears that complete exchange should take place in a matter of seconds. A very long exchange time can preclude the use of a reaction because this leads to a large variation in height equivalent of theoretical plate and column holdup which is intolerable, as mentioned earlier. In some cases the reaction can be catalyzed as in the very slow exchanges

$$CO_2^{16} + 2H_2O^{18} \rightleftarrows CO_2^{18} + 2H_2O^{16}$$

and

$$C^{13}O_2 + HC^{12}O_3^- \rightleftarrows C^{12}O_2 + HC^{13}O_3^-.$$

The slow process in both of these reactions is the rate of hydration of CO_2 as represented by (*a*) and (*b*).

$$CO_2 \text{ (dissolved)} + H_2O \rightleftarrows H_2CO_3 \qquad (a)$$

$$CO_2 \text{ (dissolved)} + OH^- \rightleftarrows HCO_3^-. \qquad (b)$$

Reaction (*a*) predominates in solutions with a pH below 8, whereas reaction (*b*) predominates at a pH above 10. Reid & Urey (16) found that the rate of reaction (*a*) could be increased four to five times and the rate of reaction (*b*) up to 2,000 times by heterogeneous catalysis (etched pyrex, etc.). Hawkings, Graham, Harkness & Thode (17) were able to show that the rate of reaction (*a*) could be increased at least 2,000 times by the use of a small amount of the enzyme catalyst, carbonic anhydrase, discovered in 1932 by Meldrum & Roughton (18). Thus catalyzed, the CO_2 exchange reactions noted above offer greater promise of usefulness in separating O^{18} and C^{13}. At the present time it appears that C^{13} can more readily be prepared using the exchange between CN^- and HCN. Oxygen-18 is being enriched by thermal diffusion in small quantities by Nier.

The general problem of the rate of exchange in isotopic exchange reactions has received considerable attention in recent years because of its importance in tracer studies with radioisotopes. The information is also sought for its value in the study of bond character in chelated and other co-ordination entities [see Fernelius (19)]. Some benefit thus accrues to the related study of isotope separation.

The third criterion concerns the equilibrium constant for the isotopic exchange reactions. Urey (20, 21) and others (22) have led the way in demonstrating how these equilibrium constants can be calculated from spectroscopic data. Since the translational and rotational partition functions are classical at room temperature in all cases except for hydrogen, we are concerned solely with the vibrational function. Bigeleisen & Mayer (22) have pointed out several simplifying cancellations which take place in calculating ratios of partition functions for isotopic equilibria, and they have devised a relatively simple formula for polyatomic symetrical molecules containing isotopes of a heavy element. The authors also show that for a large separative effect it is necessary to equilibrate one compound which has high frequencies and large frequency shifts on isotopic substitution with another compound with low frequencies and small frequency shifts. This is a useful qualitative rule in devising new exchange systems for isotope separation.

The extent to which the equilibrium constant differs from unity is an exceptionally critical factor affecting the usefulness of a particular system. This difference, ϵ (or $\alpha - 1$) affects both the height, or required number of stages, and width, or required throughput, so that in its simplest aspect the plant size can be considered to be proportional to the reciprocal of the square of ϵ. Various quantitative aspects of isotope separation plant design have been derived by Cohen (23, 24) and his co-workers, and these formulae can be applied to chemical exchange plants. Some extremely versatile equations which are useful for this purpose have also been presented by Shacter & Garrett (25).

The final criterion to be met, of achieving reflux at top or bottom (or both), is essentially the chemical problem of converting the element in question from one chemical form to another. Here again, Urey's process for enriching N^{15} provides an excellent example. The nitrogen present as am-

monium ion in the liquid phase is converted to ammonia gas by treatment with caustic. The ammonia gas then travels back up the column to the top where it can then be reconverted to ammonium ion with acid. The net result of these chemical processes is the neutralization of an acid with a base to produce a salt. Benedict (26) has pointed out that this net process and the acid and caustic chemicals used correspond to the power costs or energy costs in other types of separation plants. Because of the large reflux ratio, or ratio of interstage flow, required in an isotope separation plant, large

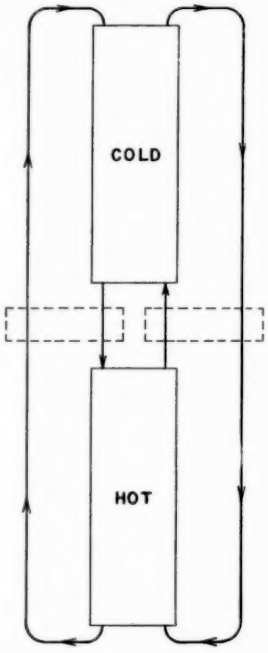

FIG. 2. Tower arrangement for avoiding the need for reflux in an isotope separation system.

quantities of chemicals are required usually in this reflux operation. Dependent upon the chemistry involved, equipment must be devised for each different process to accomplish this reflux. It must be done quantitatively with a minimum of holdup.

Sometimes the chemistry of a particular system is such as to make it difficult, if not impossible, to attain this satisfactorily. For these cases it is important to note that a means of obviating the need for reflux has been proposed by Spevak (27) which is based upon the temperature coefficient of the separation factor. By suitable selection of T_1 and T_2, we can have two towers, a hot tower and a cold tower, operating with two different separation factors. Figure 2 shows how these towers are then connected. If the large factor of the cold tower favors the incoming stream at the top, then

the smaller factor of the hot tower favors this same stream somewhat less as it emerges from the bottom of the hot tower. Thus, we have a buildup of desirable component between the two towers as shown in this diagram. The hot tower acts somewhat as a reflux mechanism since it prevents the exit from the system of desirable component by means of its smaller separation factor. Since this eliminates the need for large amounts of chemicals in the ordinary type reflux device, one might conclude that this dual temperature method would have somewhat of an advantage. However, this ease of reflux is counterbalanced more or less by the fact that a much larger plant must be built and operated because of the much lower net factor using the dual temperature process which leads to a larger number of stages and a much greater interstage flow.

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ISOTOPIC TRACERS IN CHEMICAL SYSTEMS[1]

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The study of chemical problems with radioactive and enriched stable isotopes as tracers is rapidly gaining in popularity, consonant with increasing availability of tracer nuclides and their compounds, and with increasing educational impetus to nuclear chemistry. Although the applications of tracers have been greatly diverse in nature, emphasis has been largely on studies which are peculiarly susceptible to tracer techniques, so that, fortunately, the often more precise conventional techniques of chemistry seem not likely to be supplanted in the near future. In keeping with this tendency, this review will consider, for the most part, those chemical reactions and interactions whose mechanisms, rates, or equilibria have been subject to elucidation only by the specific techniques of isotope tracing. Prominent among these are isotopic exchange reactions, isotope effects in chemical reactions, molecular decomposition and rearrangement, and the phenomena of sorption and diffusion.

Although our theme will be the positive side of tracer chemistry, some of the material presented here clearly calls attention to pitfalls in the use of tracers in chemical systems. To indicate a few of the more important ones: (*a*) An undetected isotopic exchange can lead to erroneous conclusions; many of these reactions have been found to proceed at surprising rates (e.g., the heterogeneous catalysis of some electron transfer reactions), so that no *prima facie* assumptions seem safe; (*b*) differences in reaction rates of normal and tracer components can be seriously misleading, unless proper allowances are made; in chemical reactions, these differences are, of course, insignificant with the heavier nuclides, but are appreciable with carbon and lower atomic number elements in specific types of reactions; in diffusion processes even the heavier elements may show significant isotope effects; (*c*) too little attention may be given to possible effects of the ubiquitous ionizing radiations and recoil atoms in radioactive tracer experiments; even the softest beta particle or gamma ray can rupture many chemical bonds, producing highly reactive fragments; (*d*) studies of chemical systems at extreme dilution are subject to careful examination until much more is known about the physical peculiarities of "carrier-free" tracers; (*e*) the concept of purity assumes a quantitatively new meaning in tracer chemistry, since contamination of far less than 10^{-6} per cent, not detectable by conventional purity criteria, can suggest entirely erroneous conclusions; this applies not only to contamination of one nuclide by another, but perhaps more significantly to the contamination of a given nuclide in one chemical form by that in another.

Some of these problems and their implications are discussed by Yankwich

[1] This review is essentially a survey of papers published in 1950.

(240). It seems imperative that studies of these basic nuclear-chemical processes keep abreast of the applications of tracers to chemistry. Perhaps a healthy sign is that some of these effects are becoming well enough understood that they themselves are serving useful roles in applied nuclear chemistry. For example, isotopic exchange rates have been correlated with molecular structure and dissociation, and their study has begun to yield valuable information on the mechanisms of ionic interactions in solution. Useful tracer compounds have been made by exchange reactions (68, 226). Studies of isotopic exchange and isotope effects have made a considerable contribution to the field of reaction kinetics, placing current theory on firmer ground. The isotope effect itself has been used (158) as a tool in an exploration of the mechanism of aromatic substitution. The study of radiation-induced chemical change has become a valuable adjunct of photochemistry and of radiation biology, and even recoil atoms have been put to work in a unique study (73) of surface phenomena. The behavior of surface-active agents is being studied radiochemically, as are many problems of radiocolloid formation at high dilution. One can hope that further investigation of the purity problem will also be fruitful, leading to the establishment of some useful criteria for extreme purity.

Brief reviews of the general field of applied radiochemistry have been published recently by Schacht (197) and Maddock (150). Other reviews more specific in nature are referred to in the appropriate sections. The extensive reviews and discussions of the field by Hahn (87), Paneth (180), and Seaborg (202) have been supplemented in recent years by the books, more restricted in scope, of Calvin *et al.* (42) and Broda (31). Some review and much valuable information on techniques and procedures is given by Friedlander & Kennedy (74), Schweitzer & Whitney (201), and Williams (234). Although dealing largely with biological systems, the books by Kamen (119), Hevesy (101), and Siri (205) discuss the general aspects of tracer techniques. It is hoped that the comprehensive review edited by Wahl & Bonner (224), soon to be published, will fill the unavoidable gap between this and earlier treatments of the subject.

Isotopic Exchange Reactions

Reactions involving the interchange in chemical state between two atoms of the same element may best be studied by the tracing of isotopes. Such reactions may involve an actual exchange of atoms between bound (or bound and unbound) states, as, for example, the exchange of Cl between HCl and Cl_2; or the exchange may be only apparent, as in the exchange of manganate and permanganate ions, where the isotopic label may be shifted from one chemical form to the other by the transfer of an electron. Review and discussion of isotopic exchange will be found in the two 1948 symposia, held in Paris (49) and at Brookhaven (35).[2]

[2] Since preparation of this manuscript, a splendid review of this subject by Haissinsky (88a) has been published.

Inorganic exchange reactions and their relationship to bond type have been reviewed by Haissinsky & Daudel (91). These authors classify such reactions, according to mechanism, into two principal types: (*a*) those which involve the formation of an intermediate complex, or reactions by association, and (*b*) those which are effected by decomposition of one or more of the normal components of the system, or reactions by dissociation. While this classification will be useful as a guide in our general discussion of the mechanisms of exchange reactions, ignorance dictates a more commonplace grouping in the description of individual reactions.

Mechanisms of isotopic exchange.—Considering an exchange reaction described by the general equation

$$AX^* + BX = AX + BX^*$$

where X* is a physically distinguishable isotope of X, the mechanism of exchange by association involves formation of an intermediate complex AX*XB, which may dissociate either to AX* or to BX*. This complex may, of course, be either stable and isolable, or unstable and transitory. In any case, however, a close approach of the interacting species is required. Presumably following some variation of this mechanism are (*a*) electron transfer reactions (e.g., Fe^{II}-Fe^{III}), (*b*) intermolecular atom-transfer reactions in cases where dissociation is slight (e.g., exchange of N between NO and NO_2 through the equilibrium with N_2O_3), and (*c*) molecular rearrangement reactions, in which the intermediate complex will generally have little existence value (e.g., a Walden inversion process).

Exchange by dissociation follows axiomatically if the species X and X* assume identical chemical forms in the system. This will occur between AX* and BX if both are appreciably dissociated, and between AX* and X if the former dissociates. Examples are seen in the exchange of oxygen between water and acids, as in the equilibrium

$$H_2CrO_4 = CrO_3 + H_2O,$$

and in the exchange of halogens with polyhalides,

$$PCl_5 = PCl_3 + Cl_2.$$

As a subgroup in this classification reversible reactions involving a third species should be included; for example, the exchange of arsenic between arsenate and arsenite ions in acid solution is measurably fast only in the presence of iodine or iodide ion, probably proceeding via the reversible equilibrium

$$H_3AsO_4 + 2I^- + 2H_3O^+ = H_3AsO_3 + I_2 + 3H_2O.$$

Atomic transfer reactions.—The multiplicity of structural factors influencing rates of atomic transfer reactions is discussed by Haissinsky & Daudel (91), Pauling (183), and Kamen, Kennedy, & Myers (120). Exchange by association will be limited by the geometrical involvement of the atom in question, as indicated by the work of Ingold (108) demonstrating a sharp

drop in exchange rate between bromide ion and alkyl bromides on ascending the series from methyl to neopentyl bromide. Exchange by dissociation, limited primarily by the equilibrium degree of dissociation, will also be somewhat dependent (for a given bond type) on the number of co-ordinated groups.

Qualitatively, relationship of atomic exchange rates to bond type seems well-established at the ionic and covalent extremes, since many observed reactions are fast at the former and slow at the latter. Considering the ferric iron complexes, for example, the ionic extreme $^6\Sigma$, is exemplified by the trisoxalate complex (which is forbidden resonance with the normal covalent state $^2\Sigma$), exhibiting rapid exchange of oxalate ion with oxalic acid in aqueous solution (85). The covalent extreme is well-represented by ferricyanide ion which does not readily exchange cyanide ion with its environment (3). Between these extremes many covalent bonds with partial ionic character (182) exhibit exchange rates which seem to be correlated positively with the amount of ionic character. This correlation, with bonds of a given type, would follow from the expected relationship between degree of dissociation and amount of ionic character in a series of structurally similar molecules or ions whose dissociation products exhibit similar solvation energies. With oxygen-bearing anions in neutral or acid solution (91), exchange of oxygen with water is measurably rapid for many whose central atoms differ in electronegativity from oxygen by one unit or more, corresponding to greater than 20 per cent ionic character for the bond (e.g., $SiO_3^=$, $CrO_4^=$, $PO_4^{\equiv}$, $CO_3^=$, and $SO_3^=$); in four cases where the bond is calculated to be less than 5 per cent ionic (NO_3^-, NO_2^-, ClO_4^-, ClO_3^-), exchange is immeasurably slow.[3] That the correlation of exchange velocity with bond type is not rigorous, however, is seen in many examples; if dissociation is energetically favored by solvation (or solvolysis) or by geometrical factors, or if a reversible equilibrium involving an associated complex is established, rapid exchange can occur even with essentially covalent bonds. As an example, exchange of halide ions with free halogens ("pure" covalent bonds) can occur by a variety of mechanisms: (*a*) dissociation to atoms; (*b*) dissociation to ions X^+ and X^-; (*c*) hydrolysis, to yield HOX and X^-; or (*d*) formation of the complex X_3^-, where all atoms are equivalent. Similarly, such complexes as $HgI_4^=$, involving weakly bound ligands, dissociate readily in solution and, consequently, show rapid exchange reactions despite a small electronegativity difference between atoms.

In the associative mechanisms of exchange, a significant factor controlling rates will be the availability and stability of extra bond orbitals. As indicated by Haissinsky & Daudel (91), PCl_3 and $AsCl_3$ with bond energies of 62.8 and 60 kcal. per mole respectively exchange Cl atoms readily with HCl; exchange is slower between HCl and $SiCl_4$ (85.8 kcal. per mole), per-

[3] In strongly acid solution, nitrate ion has been found to exchange oxygen with water at an appreciable rate (128, 238).

haps, in part, because of the greater bond energy; however, no exchange has been observed between HCl and CCl_4 (66.5 kcal. per mole). Considering the availability of stable orbitals, this is not surprising, since all four of the stable L shell orbitals (*s* and *p*) are involved in bond formation in CCl_4; the central atoms of the other compounds all have stable *p* and/or *d* orbitals with which to form more or less stable intermediates.

While some significance can be attached to each of these factors, it appears at present that atomic exchange reactions are too highly diverse in nature to be embraced by a simple, unified theory. Unfortunately, we shall arrive at a similar conclusion regarding the somewhat less complex reactions of electron transfer.

Electron transfer reactions.—Interactions in which a mutual interchange of chemical state between two isotopes of a given element occurs by a transfer of one or more electrons have been discussed by Gryder (83), Rona (194), and Haissinsky (88). Such exchanges represent the simplest type of oxidation-reduction reaction, where the free energy change is zero (in reactions occurring at equilibrium), and present a convenient approach to the study of mechanisms of oxidation-reduction reactions in which entropy changes are small.

Oxidation-reduction reactions of this type have been discussed by Gryder, who evaluates, in the light of recent exchange experiments, three factors supposedly influencing their rates: (*a*) coulombic forces between ions; (*b*) the number of electrons donated or received; and (*c*) the free energy change in the process. That coulombic forces alone are not responsible for these reaction rates is indicated by the faster exchange between cerous and ceric ions (84) than between thallous and thallic ions (188), both in perchloric acid solution. The fact that some simple exchange reactions (involving transfer of one or of a fixed number of electrons) are slow indicates that rates are not necessarily fast when the oxidant donates the number of electrons required by the reductant. Finally, the exchange rates between stannous-stannic and cerous-ceric ions ($\Delta F = O$) are considerably faster than other oxidation-reduction reactions of these systems in which large negative free energy changes occur.

Since none of these hypotheses was found satisfactory, Gryder proceeded to examine the extensive data recently collected on the thallous-thallic (62, 97, 188) and cerous-ceric (62, 84, 144) exchange systems. In the thallium system, rates have been found to vary positively with anion (nitrate) concentration, and negatively with acid strength. These findings were interpreted as a rate dependence either on the electric properties of the medium surrounding the ions, or on the activity coefficients of reactants as influenced by electrolyte concentration. The first of these hypotheses is in accord with the mechanism proposed by Haissinsky (88) whereby exchange occurs through the medium of a transitory complex formed by ionic association, i.e., a "shield" of anions permits a sufficiently close approach of the cations to allow the electron transfer. Variation of the activation entropy with nature

of the anion in the thallium system supports this hypothesis. In the cerous-ceric system, studies of the kinetics of the exchange reaction led to a postulate that an electronically activated state of cerous ion participated in the reaction. That such excitation is an important rate-controlling factor is not surprising in view of the geometrical dependence of the electron wave function on degree of excitation. Summing the factors influencing exchange rates, Gryder lists: (*a*) complex-forming ability of the exchanging species; (*b*) electronic state of the ions; (*c*) free energy of activation; (*d*) electrical properties of the solution; and (*e*) perhaps the charge product of the reacting ions in a relatively minor role.

Interesting studies of the relationship between electron transfer and the spectrochemical properties of systems containing elements in two valence states have been reported by Davidson and co-workers (36, 155, 231). Rather generally ionic solutions and solids containing Sb, Sn, or Fe in both stable oxidation states exhibit intense coloration, entirely out of proportion to the optical densities predicted for mixtures of the two ions. This increased optical density is attributed to absorption of light by interaction complexes between the pairs of ions, and such interaction complexes could provide a medium for the transfer of electrons. The reasonably fast exchange reactions observed between Sb^{III} and Sb^{V} (28), Sn^{II} and Sn^{IV} (36), and Fe^{II} and Fe^{III} (202), in HCl solutions have been attributed (231) to these interaction complexes; all of these complexes have been shown spectrochemically to be dimeric, containing one atom each of the two oxidation states and presumably a multiplicity of co-ordinated chloride ligands. In the case of Fe, the interaction absorption decreases with decreasing HCl concentration, and, in the absence of chloride ion, in perchloric acid solution, the absorption drops to that normally expected for the mixed ions; corresponding to this change, electron transfer between the iron species has been found to be slow (18, 126, 144, 221) in perchloric acid solution. Similarly, solutions of mixed Tl^{I} and Tl^{III} ions show no interaction absorption (154, 231) and exhibit only slow exchange (97, 188) of electrons. Davidson (231) suggests that the observed abnormal absorption results principally from interaction between electronically excited states of the ions involved, rather than between their ground states, and that the probability of electron transfer in such circumstances would be enhanced by the greater overlap of electronic wave functions. Evidence is reported (36) that the absorption of light by the Sn^{II} and Sn^{IV} interaction complex induces the exchange of electrons with a quantum yield of about 0.2. These interesting bits of information lend support to both the ionic association hypothesis of Haissinsky and the electronic excitation hypothesis of Gryder, discussed above. On the negative side, no interaction absorption is observed visually (36) in ferro-ferricyanide solutions, where electron transfer is rapid (47, 85, 215).

Libby (140) arrives at an account of the electron transfer mechanism involving ionic association and electron orbital overlap, and invokes the Franck-Condon principle as providing an additional barrier to fast exchange.

The hydration spheres of ions in two oxidation states in solution might well be nonidentical. Close approach of the ions, however, permits electron orbital overlap and coalescence of hydration spheres, reducing the barrier to exchange to a level which permits the reaction to proceed.

Electron transfer between structurally similar complex ions has been found to be fast if the complexing group is "conducting," i.e., provides through resonance a means of transfer of electrons between the periphery and the core of the complex, as in the apparent exchange of Fe between ferro- and ferricyanide ions (47, 85, 215). If the central atom is bound to its ligands by single or saturated bonds, however, exchange becomes measurably slow, as indicated in the experiments of Lewis *et al.* (138) on the exchange between trisethylenediamine cobalt (II) and (III), and between the hexammino complexes of the same ions.

Heterogeneous catalysis, as clearly demonstrated by Prestwood & Wahl (188) and by Lewis, Coryell & Irvine (138), is a significant rate-determining factor in electron transfer reactions. Early studies (204) of the Ce^{III}–Ce^{IV} system in nitric acid solution, in which precipitation was used as a separation procedure, led to the conclusion that exchange was instantaneous; subsequent work (62, 84), employing diffusion methods of separation, indicates a measurable rate for this transfer. In the Tl^{I}–Tl^{III} system in perchloric acid, Prestwood & Wahl demonstrated that platinum black caused a marked increase in transfer rate, and that four different precipitation methods employed for separation of the two oxidation states induced apparent exchanges due to coprecipitation or separation-induced exchange or both. In some cases, corrections may be applied for these effects in rate experiments, as described in the following section.

Kinetics of exchange reactions.—Following earlier treatments by McKay (156) and Duffield & Calvin (66), the kinetics of isotopic exchange reactions has been discussed recently by Norris (175) and by Friedlander & Kennedy (74). A simple homogeneous exchange reaction occurring at equilibrium, expressed by $AX+BX^*=AX^*+BX$, will show a simple first-order rate of transfer of X^* from the initial to the final species (neglecting isotope effects), regardless of its mechanism. The rate may, therefore, be expressed by

$$R = -\frac{2.3}{t}\left(\frac{ab}{a+b}\right)\log(1-F),$$

where a and b are the (constant) concentrations of AX and BX respectively, and F is the fraction of exchange equilibrium which has been attained at time t. As indicated by Norris, R expressed in this manner represents the total number of exchanges, labelled and unlabelled, per unit time in the concentration units employed. Hence, at equilibrium, it is independent of the tracer concentration, and remains constant throughout a run; under a given set of conditions it bears no relationship to the nature of the reaction so that its variance with temperature, concentration, and other factors must be studied by the usual techniques of reaction kinetics to elucidate the reaction

mechanism. A useful table expressing algebraically the value of F in various units, for use in measurements of a variety of types, is presented by Norris. Davidson & Sullivan (56) have described an algebraic method for estimation of the error (arising from radioassay error) as a function of the extent of the exchange, and for selection of the optimum degree of exchange for minimizing the error.

If one (or both) of the exchanging species contains more than one X atom, a more complex treatment of rates will usually be required, as described by Friedlander & Kennedy. If, in AX_n, all of the X atoms are equivalent, the first-order rate law will apply provided concentrations of X are expressed in gram atoms rather than in moles. For nonequivalent X atoms, two or more rates will be superposed, leading to a complex semilogarithmic plot which may be analyzed if the rates are reasonably disparate. Fialkov & Nazarenko (71) have pointed out that equivalence of atoms in a molecule or ion is not demonstrated by measurements showing only complete exchange, since small rate differences for nonequivalent atoms are reflected only in curvature of the rate plot. As an extreme case of a complex curve, the recent study by Ames & Willard (7) of the $SO_3^{=}$-$S_2O_3^{=}$ exchange has redemonstrated the nonequivalence of the two sulfur atoms in the thiosulfate ion.

As described by Norris, special treatment is required for heterogeneous exchange reactions. Zimens (242) presents expressions particularly applicable to exchange between solids and gases or liquids, considering cases where the exchange rate is limited by diffusion within the solid, by diffusion through a layer of gas or liquid adsorbed on the solid, or by chemical reaction at the interface. For the last two of these limiting factors, the expressions given by Norris are valid, but when solid diffusion is rate-limiting, the observed exchange rate will again be complex. An example of this type of reaction is found in the recent work of Wilzbach & Kaplan (236) on the H_2-LiH system.

Heterogeneous catalysis in an exchange reaction may be detected in many cases by determining the effect on the rate of varying the nature and amount of exposed surface, or of varying the nature of the medium. Such a reaction may deviate from the semilogarithmic function in a given run, if, for example, one species is more strongly adsorbed on vessel surfaces than the other. Correction for separation-induced exchange or other separation errors, provided these are constant within a given run, can be made by means of an equation given by Prestwood & Wahl (188):

$$F = \frac{F' - F_o'}{1 - F_o'},$$

where F is the fractional exchange in solution at time t, F′ is the observed fractional exchange at time t, and F_0' is the apparent fractional exchange at zero time.

The kinetics of gaseous exchange reactions in systems with a temperature gradient has been discussed by Waldmann (225); equations are derived to

account for concentration changes, diffusion currents, and exchange-equilibrium perturbations.

Summary of recent exchange studies —In the following brief accounts of recent significant isotopic exchange studies, reactions are classified as to chemical species traced, except for those reactions involving complex ions, which are treated as a group including exchange reactions of both central atoms and co-ordinated atoms or groups.

Hydrogen.—Hydrogen exchange reactions have been studied with stable H^2 (deuterium, D) and with the 12-year β emitter H^3 (tritium, T). Isotopic partition functions generally must be taken into account (see section on ISOTOPE EFFECTS).

Hydrogen: H_2/LiH.—This heterogeneous (gas-solid) exchange was observed (236) to proceed at a measurable rate at room temperature, and to be complete in 24 hr. at 200° showing a rate proportional to a d log (1-F)/dt, where a is the quantity of H_2. Nonlinearity of plots indicates diffusion is rate-limiting.

Hydrogen: H_2/C_2H_4.—Gaseous exchange of ethylene with two volumes of D_2 on a nickel wire at 90° proceeded (219) more rapidly than the addition reaction; the concentration of normal ethylene decreased exponentially, while that of the D-substituted ethylenes went through a maximum before reaching zero. Results suggest the possibility that ethylene hydrogenation involves hydrogen atoms that were previously on another ethylene molecule.

Hydrogen: H_2/CH_4.—In the absence of oxygen, no exchange was observed (232) between methane and HD at 476° to 515°. With oxygen present, exchange occurred during the slow combustion of methane (homogeneous reaction) at these temperatures. Apparent activation energy of the exchange was about 87 kcal. per mole.

Hydrogen: H_2/KNH_2, KOH.—Very rapid (half-time <1 min.) exchange between deuterium gas and liquid ammonia solutions (0.001 M) of potassium amide at −50° has been demonstrated (45). The exchange reaction between deuterium gas and aqueous potassium hydroxide was unaffected by light or increase in glass surface, and appeared to be first order with respect to both deuterium gas and hydroxide ion.

Hydrogen: $HCCl_3/HCBr_3$.—Exchange of hydrogen between deuterochloroform and bromoform has been studied (203) by following infrared spectra. Less than 0.1 per cent exchange occurred in seven days at 105° (in liquid or vapor phase). In the presence of organic bases the liquid phase exchange proceeded at a measurable rate, indicating a possible ionic mechanism.

Hydrogen: HBr/C_2H_5Br.—Exchange of D in DBr with all five hydrogen atoms of ethyl bromide occurred (184) between 258° and 306°, with an activation energy of 40 kcal. per mole, in a reaction first-order with respect to DBr and roughly first-order with respect to ethyl bromide.

Hydrogen: HCl/C_6H_5OH.—Hydrogen exchange between anhydrous DCl and phenol has been found (99) to be complete in several minutes at 50°, and

to involve the hydrogen atoms at the two, four, and six positions of the ring as well as the hydroxyl hydrogen.

Carbon.—In view of the tremendous number and variety of applications of tracer carbon, there is a surprising and alarming dearth of information on its isotopic exchange reactions. Of those reported here, all have employed either radioactive C^{14} or stable C^{13}.

Carbon: CO/CO_2.—Catalytic exchange of C^{14} between CO and CO_2 is reported (177) to occur at 800° to 900° at a rate proportional to the 0.73 power of CO pressure and to the 0.85 power of CO_2 pressure. The apparent activation energy was 77 kcal. per mole. The reaction was accelerated by added nitrogen, but not by argon. Results are consistent with a bimolecular exchange on the catalyst surface.

Carbon: $CO_2/BaCO_3$.—Following earlier studies (10, 239) described by Calvin *et al.* (42), the technically important loss of activity from solid $BaC^{14}O_3$ samples exposed to gaseous CO_2 has been re-examined (196). At one atmosphere of CO_2 and relative humidities of 3 per cent to 75 per cent, activity of the samples decreased 1.3 per cent to 3.5 per cent; the decrease was independent of sample thickness, but dependent on particle size. Samples heated in air to 140° lost 2.5 per cent to 3.0 per cent of their activity, but were stabilized against further exchange losses by the heating.

Carbon: $CO_3^{=}/HCO_2^{-}$.—Exchange of tracer carbon between formate and carbonate has been observed (82) incidentally in the hydrolysis of cyanides in the presence of carbonates. Additional studies with C^{13}-labeled sodium formate and with C^{13}-labeled sodium carbonate have revealed that a simple exchange, possibly involving oxalate ion, occurs.

Carbon: $HCONH_2$/formamido group.—The preparation of adenine-8-C^{13} has been accomplished (44) by C^{13}-formylation of 4,5,6-triaminopyrimidine sulfate to yield 4,6-diamino-5-formamidopyrimidine, which, on heating as the sulfate in formamide, yields the desired product. In this final step, extensive exchange between the formamido group and the formamide occurred, so that only 25 per cent of the C^{13} label appeared in the adenine. The exchange may occur through ammonolysis of the formyl group, since formamide decomposes on heating to carbon monoxide and ammonia. No exchange between adenine and formamide was observed.

Nitrogen: N_2/NH_2OH.—No exchange of N^{15} could be detected (185) between an atmosphere of nitrogen (10 per cent N^{15}) and 0.1 *M* solutions of hydroxylamine in water or buffered bacteriological culture media in 24 hr. at room temperature.

Nitrogen: NH_3/NH_4^{+}.—Equilibrium exchange of stable N^{15} in dissolved ammonium salts with the liquid ammonia solvent was observed (179) in seven minutes at the boiling point of the solvent (−33°).

Oxygen.—Exchange reactions of oxygen have been studied by mass spectrometric methods with the stable O^{18} isotope.

Oxygen: O_2/H_2O, CO_2 in electric discharge.—No exchange was observed (189) between oxygen gas and H_2O at −40° in an electric discharge; con-

siderable exchange occurred, however, with CO_2 under similar conditions. These results may bear on the enhanced O^{18} content of the atmosphere.

Oxygen: H_2O/NO_3^-.—Earlier studies have shown no oxygen exchange between nitrates and H_2O in neutral (94, 216, 238), alkaline (94) or 0.2 *M* nitric acid (94) solutions, and complete exchange in 24 hr. at 100° in 0.5 *M* sulfuric acid (238) solution. Recent work (128) reports exchange in 40 per cent HNO_3 at 30.°

Oxygen: O_2/solid oxides.—Initial rapid exchange, followed by a slower process occurred (103, 237) between oxygen gas and MgO, γ-Al_2O_3, ZnO, ThO_2, or TiO_2 at 400° to 500°. First-order rates were observed for the rapid process with the first two of these, and the activation energy for the exchange with Al_2O_3 appeared to be 37.3 kcal. per mole.

Oxygen: H_2O/solid oxides.—Rapid surface exchange followed by a diffusion-limited rate occurred between water vapor (20° to 400°) and γ-Al_2O_3, ThO_2, or TiO_2 (229), and between water vapor (100° and 565°) and silica gel or aluminum gel (160). No exchange was observed (160) between H_2O and several clays.

Phosphorus, arsenic, and antimony.—Exchange reactions of phosphorus and arsenic have been studied with the 14.0-day P^{32}, and the 27-hr. As^{76}, respectively. The 2.8-day Sb^{122} and the 60-day Sb^{124} were used in the antimony exchange reactions reported here.

Phosphorus: $(NaPO_3)_3/(NaPO_3)_6$.—No P^{32} transfer from 0.01 *M* trimetaphosphate (or its hydrolysis products) to 0.06 *M* hexametaphosphate was observed (222) in the pH range from 2.0 to 10.0 in periods up to 26 hr.

Phosphorus: H_3PO_4/phosphate esters.—In dioxane solution no exchange was observed (149) in 20 to 30 hr. at 100° to 300° between P^{32} in H_3PO_4 or Na_2HPO_4 and ethyl, *n*-butyl, isobutyl, hexyl, or tolyl phosphates.

Arsenic: $AsCl_3/AsBr_3$.—Complete exchange of As^{76} between the trichloride and the tribromide, and vice versa, is reported (164) to occur in 10 min. or less at 132° in a solution of 13 gm. of tribromide in 7 gm. of trichloride.

Antimony: $SbCl_3/SbBr_3$.—Studies similar to those just described for arsenic have indicated (164) rapid exchange of antimony between the trichloride and the tribromide at 225°.

Antimony: Sb^{III}/Sb^{V}.—In 5–6 *M* HCl solutions tri- and pentavalent antimony were found (28) to exchange at appreciable rates (half-times about 60 hr.) proportional to $(Sb^{III})^{0.6}(Sb^{V})^{1.1}(H^+)^4(Cl^-)^9$. Apparent activation energy for the exchange was 27 kcal. per mole. A half-time of 36.2 min. is reported for the exchange in 12.0 *M* HCl at 25° with (Sb^{III}) at 0.0235 *M* and (Sb^{V}) at 0.0198 *M*.

Sulfur and selenium.—Exchange experiments of sulfur and selenium have employed largely the radioactive isotopes, 87-day S^{35}, and 127-day Se^{75}, respectively.

Sulfur: S_8/Na_2S_x.—The rate of exchange of S^{35} between polysulfide and solid sulfur has been studied (93) as a function of temperature and composi-

tion of the sulfide, and found to proceed at an easily measurable rate, limited by diffusion, with an activation energy of about 47 kcal. per mole.

Sulfur: $S_c/S_2O_3^=$, $SO_4^=$.—No significant exchange was observed (162) between S^{35} in thiosulfate ion and colloidal sulfur, or vice versa, in 18 hr. at room temperature over the pH range 3.4 to 14. Under similar conditions, no appreciable exchange occurred between sulfate ion and colloidal sulfur.

Sulfur: SO_2/SO_3.—Sulfur trioxide showed (107) no appreciable sulfur exchange with its sulfur dioxide solvent in 336 hr. at room temperature, or in 72 hr. at 132°. Since these species do exchange oxygen (167) an acid-base interaction, such as

$$SO_2 + 2SO_3 = SO^{++} + S_2O_7^=,$$

is indicated.

Sulfur: $SO_2/SOCl_2$.—Thionyl chloride exchanged (111) sulfur with its SO_2 solvent slowly at ordinary temperatures (half-times about 2,000 hr.) indicating that its behavior as an acid may be somewhat overrated.

Sulfur: $SO_2/(Me_4N)_2SO_3$.—Complete exchange in less than 2.5 hr. is reported (111) for S^{35} in tetramethylammonium pyrosulfite with liquid SO_2.

Sulfur: SO_2/H_2SO_4.—The exchange of sulfur dioxide with concentrated (97.2 per cent) H_2SO_4 has been studied (176) in sealed tubes at room temperature, 101° and 211°, and showed half-times of greater than 27 years, 1.6 years, and 7.5 years, respectively. Apparent activation energy was 22.0 kcal. per mole.

Sulfur: $SO_3^=/S_2O_3^=$.—Kinetics of the sulfite-thiosulfate exchange has been restudied (7), confirming earlier exploratory work. Rate was proportional to the first power of gross sulfite concentration and to the first power of thiosulfate concentration, and the activation energy was between 14 and 15 kcal. per mole. Only one sulfur atom of the thiosulfate ion exchanged in five hours at temperatures up to 125°.

Sulfur: H_2S/CS_2.—Following a report (68) that aqueous sulfides exchanged sulfur with CS_2 as a separate phase (probably through the thiocarbonate ion), it has been reported (64) that no observable exchange occurred between H_2S and CS_2 in benzene solution in 95 hr. at 120°.

Selenium: Se/Se^{IV}.—Exchange of Se^{75} between amphorous solid Se and HCl solutions of SeO_2 has been found (92) to proceed rapidly at acid concentrations greater than 7 *N*, reaching a value near 40 per cent completion in one hour at about 10 *N* HCl. Apparent activation energy was 6 kcal. per mole.

Selenium: $Se/Se^=$.—Exchange between amorphous Se and polyselenide ions proceeded rapidly (92) at 0°, approaching half completion in 14 min. for the diselenide. The reaction was somewhat slower at 18°, and was dependent on the value of x in Na_2Se_x.

Halogens.—Halogen exchange reactions, except for those of fluorine, have been studied quite extensively with a variety of tracers including 2×10^6-year Cl^{36}, 38-min. Cl^{38}, the 4.4-hr.-18-min. $Br.^{80}$ pair, 34-hr. Br^{82}, and 8.0-day

I^{131}. For fluorine, the longest-lived radioisotope is the 112 min. positron emitter F^{18}.

Halogens: I/I_2.—The rate of the exchange of iodine atoms with iodine molecules in hexane solution at 25° has been estimated (178) from indirect studies involving the exchange reaction between I atoms and *trans*-diiodoethylene. The rate constant was found to be about 8×10^{10} ml. $mole^{-1}$ $sec.^{-1}$, and the activation energy was indirectly estimated to lie between 2 and 3 kcal. per mole.

Halogens: HX/X_2.—The gaseous exchange of halogens with hydrogen halides has been observed to proceed rapidly at ordinary temperatures for chlorine (58) and bromine (109) (half-time 0.14 to 0.75 sec. at 1 mm.). A heterogeneous reaction in bromine exchange has been demonstrated (109) by the increase in rate (half-time 0.06 to 0.08 sec.) induced by the addition of silica wool to the system. The chlorine reaction has been observed (114) to proceed much more slowly (17-hr. half-time at 0.04 atm.) in fluorocarbon-coated vessels, indicating a heterogeneous mechanism for this exchange. The corresponding fluorine species did not exchange (58) at an appreciable rate at room temperature but showed appreciable exchange at 200° in an hour; this reaction also appeared to be heterogeneous, occurring on the walls of the brass vessel.

Halogens: $AlCl_3/CCl_4$, other halides.—The exchange of Cl^{36} in dry solid $AlCl_3$ with liquid CCl_4 has been observed (100, 226) to proceed rapidly to 15 per cent completion at −21° and to 40 per cent completion at 25°. The reaction proceeded to completion only at temperatures above 75°, however, apparently occurring only on the surface of the solid at the lower temperatures. After the $AlCl_3$ had been exposed to moisture, the reaction proceeded (slowly) only at the higher temperatures. Similar exchange reactions of $AlCl_3$ have been observed with chloroform, the three isomeric butyl chlorides, and *n*-amyl chloride, providing a convenient means of preparing tagged forms of these compounds.

Consistent with the hypothesis of exchange on the $AlCl_3$ surface are results (27) showing exchange of Cl^{36} between $AlCl_3$ and gaseous chlorides (CCl_4, chloroform, and ethyl, *n*-butyl, *n*-amyl, and benzyl chlorides). A Friedel-Crafts reaction between gaseous CCl_4 and benzene on the $AlCl_3$ surface was observed in connection with these experiments.

Halogens: ClO_2/ClO_2^-, etc.—Rapid exchange was observed (59) between ClO_2 and chlorite ion in neutral aqueous solutions. At low concentrations (10^{-4} *M*) the rate was slow enough to be measurable. No exchange of Cl between ClO_2 and perchlorate or chlorate ions, or molecular or atomic chlorine was observed. A slow exchange occurred between HOCl and ClO_2 concurrently with the oxidation of ClO_2 to chlorate.

Halogens: I_2/IO_3^-.—Kinetics of the iodine-iodate exchange reaction has been very thoroughly studied (51, 165) and the exchange has been shown to proceed via the reversible reaction between IO_3^- and I^-. The rate was proportional to $(I_2)^{0.6}(H^+)^{1.8}(IO_3^-)^{0.8}$. The activation energy was found (165)

to be 19–22 kcal. per mole. The salt effect and effect of ionic strength were also studied and the rate constant evaluated. Typical half-periods observed were about 450 hr. at 10^{-3} *M* I_2 and 0.088 *M* HIO_3, and about 8.7 hr. at 10^{-3} *M* I_2 and 0.5 *M* HIO_3 (25°).

Halogens: $Br_2/HgBr_2$.—At temperatures slightly below 0°, Br^{82} in Br_2 was found (65) to exchange completely with $HgBr_2$ in carbon disulfide solution in less than 2.5 min.

Halogens: $Br_2/HgBr_4^=$.—Equivalence of the four Br atoms in $HgBr_4^=$ is claimed (71) on the basis of studies of exchange of Br between K_2HgBr_4 and Br_2 in sealed tubes at 250°, followed to 25 per cent of the equilibrium value.

Halogens: Br_2, HBr/C_2H_5Br.—A study (184) of systems containing radioactive Br_2 and ethyl bromide at temperatures up to 350° indicated that no direct thermal exchange reaction occurs between these species. Hydrogen bromide, however, exchanges Br with ethyl bromide between 180° and 310°, with an activation energy of about 32 kcal. per mole, in a reaction which is first-order with respect to ethyl bromide and zero-order with respect to HBr, and at a rate depending on the nature and amount of surface present.

Halogens: Br_2/Cl_3CBr.—Kinetic studies (55) of the gaseous exchange between radioactive bromine and trichlorobromomethane in the range 147° to 180° revealed rate dependence on the square root of bromine pressure and the first power of Cl_3CBr pressure. The rate constant was evaluated:

$$\log_{10} k = \frac{-33{,}100(\pm 400)}{4.574T} + 12.75(\pm 0.20),$$

and the activation energy for the elementary reaction involving bromine atoms was 10.3 kcal. per mole. A free radical mechanism was proposed.

Halogens: Br^-/Diethyl bromoethylmalonates.—Rates of exchange of α, β and γ diethyl bromoethylmalonates with bromide ion in absolute acetone have been studied (137) and showed rate constants (25°), respectively, of 0.5, 70, and 12 liter $mole^{-1}$ $hr.^{-1}$. Activation energies for the exchange reactions of the β and γ compounds were 13.5 and 17.5 kcal. per mole, respectively.

Halogen: NaI/C_2H_5I.—Kinetics of the exchange of a "long-lived" radioactive iodine isotope between sodium iodide and ethyl iodide in alcohol solution has been studied (168), and the second-order rate constant evaluated at 10°, 20°, 30°, 40°, and 80° as $10^4k = 0.23$, 0.92, 2.15, 4.2, and 153 liter $mole^{-1}$ $sec.^{-1}$, respectively, corresponding to an activation energy of 19.0 kcal. per mole.

Halogens: Br/allylic or vinylic halides.—Efficient exchange of bromine atoms (produced by neutron capture reactions) with Br in allylic and vinylic halides in both gaseous and liquid states has been demonstrated (96), providing a convenient criterion for the atomic condition of radioactive bromine.

Vanadium: $VO^{++}/V(OH)_4^+$.—Exchange of the 16-day V^{48} between vanadyl and pervanadyl ions was found (78, 214) to be complete in less than one minute at room temperature in 0.6 and 0.9 *M* $HClO_4$, and in 7 *M* HCl. Separation-induced exchange could not be entirely ruled out.

Chromium: Cr^{III}/Cr^{VI}.—Very slow exchange of 26.5-day Cr^{51} (<10 per cent in 12 days) is reported (37) for Cr^{51} as Cr^{III} with dichromate or chromate ions in strongly acidic or strongly alkaline solutions at room temperature, with both species at concentrations of 0.036 *M*.

Manganese: $MnO_4^-/MnO_4^=$.—Separation by solvent extraction indicated (102) that an immeasurably rapid electron transfer reaction occurs between manganate and permanganate ions in 3.5 or 4 *M* aqueous potassium hydroxide solution at 0°. This confirms earlier experiments (139) in which the two species were separated by precipitation. The 2.5-hr. Mn^{56} was used as tracer.

Manganese: MnO_2/MnO_4^-.—No exchange of Mn^{56} was observed (33) between MnO_4^- and colloidal MnO_2 at room temperature, and only slight exchange was noted after prolonged boiling.

Iron.—Exchange experiments of iron have been studied with the 4-yr. Fe^{55} (K capture) and with the 47-day Fe^{59} (β-emitter).

Iron: Fe^{II}/Fe^{III}.—Agreement seems to be general that ferrous and ferric species exchange electrons rapidly (202) in hydrochloric acid solutions. Disparate results are reported, however, for this exchange in perchloric acid solutions in experiments which attempted to eliminate catalytic effects. Van Alten & Rice (221), using a diffusion separation procedure, first reported a half-period of about 18.5 days for the reaction in 3 *M* perchloric acid at a total iron concentration of 0.023 *M*. Linnenbom & Wahl (144) attempted to reproduce these conditions and also studied other concentrations, employing the same separation procedure, and found complete exchange in one to two hours. Half-periods up to 166 days are reported by Kierstead (126), who also employed the diffusion separation method; poor reproducibility in these experiments was attributed to variations in concentrations of important trace impurities, and the uncatalyzed exchange was suspected of being extremely slow. Betts, Gilmour & Leigh (18) find, with Linnenbom & Wahl, complete exchange in the diffusion period under like solution conditions, employing the same separation procedure.

Dodson (60) studied this exchange, using a separation procedure in which Fe^{II} was complexed with α, α'-dipyridyl and Fe^{III} was then removed as the hydroxide, a process resulting in only a small amount of induced exchange; half-times between 15 and 45 sec. were observed for the exchange at perchloric acid concentrations of 0.4 to 3.0, and Fe^{II} and Fe^{III} concentrations between 0.5 and 1.1 *M*. Added traces of chloride ion showed no influence on the rate, whose second-order constant appeared to be 16 liter $mole^{-1}$ $sec.^{-1}$ in 0.4 *M* $HClO_4$ at 23°.

Tin: Sn^{II}/Sn^{IV}.—Experiments with the 105-day Sn^{113} have indicated (231) a half-period of about seven minutes for the exchange reaction between stannous and stannic forms in 9 *M* HCl, with both species at concentrations 0.1 *M*. Other studies (36) at 0° and 25° led to a rate, for the dark reaction, expressed by:

$$R = (4.5 \times 10^7)(Sn^{II})(Sn^{IV})e^{-10,800/RT} \text{ moles liter}^{-1} \text{ min.}^{-1}.$$

Rate constants at 25° were 0.38, 0.55, and 0.73 liter mole^{-1} min.$^{-1}$ at acid concentrations of 9.0, 10.0, and 11.0 *M*, respectively. Light-induced exchange is reported to occur with a quantum yield of about 0.2.

Cerium.—Cerium exchange reactions have been studied with 30-day Ce^{141} and 275-day Ce^{144}.

Cerium: Ce^{III}/Ce^{IV}.—Exchange studies employing diffusion procedures for separating cerous and ceric ions have indicated (84, 144) complete exchange in diffusion periods ranging from one to four hours in solutions 1–6 *M* in sulfuric or perchloric acids, with the cerium species at 0.005 to 0.1 *M*. A study (84) of the exchange in 6.2 *M* nitric acid solution, using a solvent extraction separation, indicated a (typical) half-time of 20 min. at 0°, with the cerous species at 0.00198 *M* and the ceric at 0.0187 *M*. The experimental activation energy was 13.4 kcal. per mole, and the reaction was first-order with respect to both cerium forms. In perchloric acid, the data are reported (62) to suggest a path in which the rate is independent of Ce^{IV}, and this is interpreted as indicating participation of an excited state of cerous ion in the exchange.

Mercury.—Mercury exchange studies have employed the β-emitting 46-day Hg^{203}.

Mercury: Hg/Hg^{II}.—In a typical experiment (89, 90), metallic mercury was agitated with a 0.1 *M* solution of mercuric nitrate at room temperature, and the exchange was found to be 20 per cent complete in 10 min. Activation energy for the exchange was 3.2 kcal. per mole.

Mercury: Hg^{I}/Hg^{II}.—Earlier studies (202) have indicated rapid exchange for mercurous and mercuric ions in aqueous solution. A restudy (127) of the system, employing a variety of separation techniques, indicates a rapid homogeneous exchange reaction, despite the presumed necessity of breaking the Hg—Hg bond in the mercurous ion; the possibility of separation-induced exchange was not entirely obviated.

Mercury: $HgCl_2/HgCl$.—Following the observation that mercury exchanges completely within one minute between mercuric acetate and phenyl mercuric acetate in a variety of solvents, studies (52) were made of the analegous chloride system in benzene solution. The two species were present in equimolar concentrations (0.01 *M*), and half-times of the order of 37 min. were obtained at 25° in either wet or dry benzene; the rate was greatly increased by the addition of hydrochloric acid.

Thallium.—The range of thallium reactions available for radiochemical study has been considerably increased by the availability of the 3.5-year Tl^{204}, which was used in the experiments described here.

Thallium: Tl^{I}/Tl^{III}.—Simultaneous reports (61, 97, 187) from two laboratories showed that the thallous-thallic exchange reaction in perchloric acid solutions proceeds at a convenient rate. When corrected for separation induced exchange, the data of Prestwood & Wahl (187, 188) indicate an exchange rate given by:

$$R = (Tl^{I})(Tl^{III})\left[k + \frac{k'}{(H^{+})} + k''(NO_3^{-})\right],$$

holding for 0.8 to 3.5 *M* $HClO_4$, 0.0 to 0.4 *M* $NaNO_3$, 10–25 m*M* $TlClO_4$, 5–25 m*M* Tl $(ClO_4)_3$, and an ionic strength (adjusted with $NaClO_4$) of 3.68 in the temperature range 10° to 50°. Harbottle & Dodson (97) report for 0.4 *M* perchloric acid solutions, thallous concentrations 0.003 to 0.015, and thallic concentrations 0.0006 to 0.003 *M*, an exchange proportional to the first power of each reactant concentration, a rate constant of 2.0 liter $mole^{-1}$ $hr.^{-1}$ at 49.5°, and an activation energy of 12 kcal. per mole. In varying acid concentration the rate constant showed a maximum at about 1 *M*. The exchange rate appeared to be significantly greater in hydrochloric acid solutions.

Observation (154) of the lack of exchange of thallous and thallic ions in solid thallium sequihalides (Tl_2Cl_3, Tl_2Br_3) has indicated that the two thallium species do not occupy equivalent crystal positions.

Uranium: U^{IV}/U^{VI}.—Studied (193) with U^{233}, the exchange of uranium between the tetra- and hexavalent states in hydrochloric acid solutions proceeded at a rate which was first-order with respect to (U^{VI}), second-order with respect to (U^{IV}), and minus third-order with respect to hydrogen ion concentration. The rate was independent of added salt, chloride ion, and illumination, and showed an activation energy of 33.4 kcal. per mole. A mechanism involving a dimeric intermediate is proposed to satisfy the observations.

Complex ions.—Aqueous cobaltous and cobaltic ions have been found to exchange water rapidly with their solvent in studies (76) with O^{18} as tracer. Aqueous chromic ion (106), however, exchanged water at a much slower rate, showing a half-time of about 40 hours in perchlorate solutions. Aquo complexes of Cr have been found (78) to exchange chromium poorly, if at all, with dichromate ion, hexathiocyanato chromium (III), and trisoxalato chromium (III) complexes, but at an appreciable rate with hexacyano chromium (III) ion.

Cyanide exchange between complex ions and aqueous cyanide solutions at pH 10 has been studied (3) with the cyanide complexes of Ni^{II}, Pd^{II}, Hg^{II}, Mn^{III}, Fe^{II}, Fe^{III}, Cr^{III}, Co^{III}, and Mo^{IV}, employing C^{14} as tracer. Exchange was immeasurably rapid with the tetracyanides, but measurable in the case of hexacyanomanganate (III), and immeasurably slow for the other cases. Photocatalysis was observed for the molybdenum complex, and acid-induced exchange was noted (pH 2 to 4) for ferrocyanide. Further studies (146) with the Ni^{II} complex have confirmed the rapid exchange, and indicated nonequivalent Ni atoms in solid nickel cyanide. Exchange of Ni^{II} between the cyanide complex and its complexes with ammonia, ethylenediamine, oxalate, and tartrate has been examined and found (146) to proceed rapidly for the first two, slowly for the others. Rapid exchange between ferro- and ferricyanide ions has been demonstrated in three experiments (47, 85, 215), and

absence of exchange between ferric ion and ferro- or ferricyanide has been redemonstrated (85).

Slow exchange is reported (153) for cobalt in its di- and trivalent ammonia complexes. A thorough kinetic study of this system, and of the Co^{II}–Co^{III} trisethylenediamine complexes is reported (138). Half-times of the latter exchange were between 2 and 50 hr. Cross reactions between the ammino and trisethylenediamine complexes, involving free-energy changes, were found to proceed much more rapidly (half-time about 4 min.) when a free-energy decrease was involved, and much more slowly for the corresponding reaction with free-energy increase.

Oxalate complexes of ferric iron are reported (85) to exchange Fe^{III} rapidly with solutions of "free" ferric ion, but not with the cyanide complexes of iron. Exchange of oxalate ion between oxalatopentammino cobalt (III) and unbound oxalate has been studied (121), and found to be immeasurably slow at room temperature, but to proceed at a convenient rate at 70° to 90°.

Exchange of carbonate ion between sodium carbonate solution and carbonato-tetrammine cobalt (III) ion has been found (98) to be surprisingly slow in view of the instability of carbonato complexes, showing a half-time of about seven hours in a solution 0.03 *M* in the complex and 0.01 *M* in carbonate.

Isotope Effects

Effects of variable isotopic composition of molecules may significantly influence results of many tracer studies. Such effects are of particular importance with the lighter elements, where the mass difference between isotopes is large relative to the total atomic masses; with the exception of spectroscopy, common experimental procedures are not sufficiently precise to detect isotope effects in the heavier elements. Among the most striking recent observations are those of Alexander & Pinkus (6), Eliel (69), and Alexander (5), who detected optical activity in several compounds whose molecules contained no centers of asymmetry except those created by the substitution of deuterium for hydrogen. Studies of the crystal structure of D-substituted KH_2AsO_4 by Dickson & Ubbelohde (57) have revealed a lattice expansion in the direction of the short hydrogen bonds attributable to the heavy isotope.

Variations of the fundamental thermodynamic functions in the isotopes of hydrogen, the most extreme case, have been given considerable theoretical study. Giauque (79) has calculated the entropy and free energy of protium, and Johnston & Long (113) have made similar calculations for deuterium (D_2) and hydrogen deuteride (HD). More recently Jones (115) has calculated the heat capacity, entropy, internal energy, and free energy of tritium and HT. These quantities may be employed in calculating the equilibrium constant of the simple isotopic exchange reaction[4] $H_2+T_2=2HT$, and values

[4] A general treatment of the calculation of such constants is given by Bigeleisen & Mayer (26).

ranging from 0.242 at 50°K. to 3.99 at 2,500°K. are obtained, strikingly illustrating an isotope effect in chemical equilibrium; the value of this constant for 25°C., calculated at 2.57, was roughly confirmed experimentally in studies of the isotope effect in bond rupture of the hydrogen species on electron impact, described by Schaeffer & Hastings (198). Similar estimations of the dissociation and exchange equilibria of the tritium halides have been made by Bigeleisen (19), from calculated ratios of the partition functions of the tritium halides to those of their respective protium halides. Illustrating the direct experimental approach to these thermodynamic isotope effects is an experiment of Suess (211), who determined the equilibrium distribution of deuterium between water and hydrogen gas, demonstrating that the equilibrium constants for the exchange reactions $HDO+H_2=HD+H_2O$, and $D_2O+HD=HDO+D_2$ are essentially equal and expressed by $\log K = (928/4.57T)-0.1320$.

Reflection of the isotopic dependence of equilibrium constants in reaction rate constants is of significance in tracer studies. Yankwich (240) presents a lucid discussion of the effect of isotopic substitution in several simple reactions. A general statistical treatment of relative reaction velocities of isotopic molecules, based on the Eyring (81) theory of absolute reaction rates, is presented by Bigeleisen (21), who formulates the rate constant ratio and expresses differences in activation energy of normal and isotopic molecules. A slightly different treatment in terms of the same theory is given by Melander (158). Wilcox (233) discusses the possibility of an additional effect attributable to "isotopic pseudoasymmetry" in a molecule which is asymmetric with respect to the isotopic species.

As discussed by Bothner-By *et al.* (29) isotope effects in reaction rates may be attributed to two theoretical factors, the reduced mass effect and the zero-point energy effect. The reduced mass effect is the ratio of frequencies with which the critical bonds in the activated complexes undergo rupture, corresponding qualitatively to differences in collision frequency in classical rate theory. The zero-point energy effect is reflected in differences in activation energies of the light and heavy molecules, that for the heavy molecule generally being greater. On the basis of the Eyring (81) theory of absolute reaction rates, Bigeleisen (21) has shown that the theoretical ratio of rates in systems differing only in the isotopic composition of their components is, in the form used by Pitzer (186):

$$\frac{k}{k'} = \left(\frac{\mu'}{\mu}\right)^{1/2}\left[1 + \sum_{i}^{3N-6} G(u_i)\Delta u_i - \sum_{j}^{3N-7} G(u_j^{\ddagger})\Delta u_j^{\ddagger}\right]$$

where the reduced mass $\mu = m_1m_2/m_1+m_2$ is that associated with the atoms forming the bond to be broken, the symbol ‡ indicates the activated complex, and $u = h\nu/kT$. The function G (u) is defined by Bigeleisen & Mayer (26) as

$$G = \frac{1}{2} - \frac{1}{u} + \frac{1}{e^u - 1}.$$

Comparison of theoretical with experimental rate ratios may meet with difficulty from several sources, particularly in the estimation of u, which requires selection of a satisfactory molecular model, and in the assumption of equal transmission coefficients for normal and isotopic species inherent in the above equation.

Investigation of isotope effects on reaction velocities has only recently become popular, and comparison of theory with experimental observations is just beginning to yield some satisfaction, as illustrated in the recent studies described below. Several reactions have been studied which failed to show significant isotope effects, and these are not described in detail. Among these are the pyrolysis of adipic acid (29) and the Cannizzaro reaction and the benzoin condensation of benzaldehyde (208).

Reaction of hydrogen with chlorine.—A study of the well-known gaseous photochemical reaction between hydrogen and chlorine by Jones (116), comparing the reaction rate of H_2 with that of HT has yielded a ratio of $(1.35 \pm 0.03) \exp [(552 \pm 7)/RT]$ for k_1/k_2 where k_1 is the specific rate constant for H_2+Cl_2 and k_2 is that for $HT+Cl_2$. This ratio is considerably greater than that predicted by the theory of absolute reaction rates, perhaps because of the choice of an incorrect model, possibly because of the approximate nature of the computations.

Reaction of hydrogen iodide with methyl iodide.—Newton (172) has investigated the relative rates of reaction of hydrogen iodide and deuterium iodide with methyl iodide at 310° and 250°. The reaction ($HI+CH_3I = CH_4+I_2$) may proceed either by a direct bimolecular mechanism or through a series of free radical reactions. The isotope effect in the former path was larger than that in the free radical reaction and was the only one determined. Protium iodide reacted about 1.4 times faster than deuterium iodide at both temperatures. Choosing a simple (C—H—I—I) four-membered ring as the activated complex, the results led to a range of characteristic frequencies and transmission coefficient ratios which may be useful in predicting rate ratios in other reactions. These data have also been considered by Bigeleisen (22), who expresses the rate constant ratio as the product of a temperature-dependent and a temperature-independent term. For an activated complex with no symmetry he finds a temperature-independent factor of 1.4, agreeing with experiment.

Photochlorination of chloroform.—Rates of the photochemical chlorination of chloroform and deuterochloroform have been compared by Newton & Rollefson (173), in the temperature range −20° to 180°. The ratio of the rate constants for the normal (k_1) and isotopic (k_2) reactions was found to be $k_1/k_2 = 1.4 \pm 0.2 \exp (714 \pm 90/RT)$. Reasonable assumptions permit a satisfactory comparison of the result with that predicted by the theory of absolute reaction rates.

Oxidation of propyl alcohol.—Westheimer & Nicolaides (228) have demonstrated a markedly lower rate of chromic acid oxidation of 2-deuteropropanol-2 than of natural isopropyl alcohol, estimating the ratio of rates to be

about six. This lower oxidation rate, arising from the differences in zero-point energies of the C—H and C—D bonds indicates that the secondary hydrogen of the alcohol is removed in the rate-controlling step of the oxidation.

Decomposition of ammonium nitrate.—The reaction $NH_4NO_3 \rightarrow N_2O + 2H_2O$ has been studied by Friedman & Bigeleisen (75), who determined the isotopic constitution of the products derived from natural ammonium nitrate. The ratio

$$\frac{N_2O^{18}}{N_2O^{16}} \Big/ \frac{H_2O^{18}}{H_2O^{16}}$$

after complete decomposition of the ammonium nitrate was found to be 1.022 ± 0.003. Assuming the reaction proceeds by the successive elimination of two molecules of water from one ammonium ion and one nitrate ion, some such steady state intermediate as nitramide was proposed, and the results compared favorably with the theoretically predicted rate constant ratio. The results indicate that the preference of N_2O for O^{18} is largely attributable to the greater frequency of rupture of N—O^{16} bonds than of N—O^{18} bonds.

Cracking of propane.—Studies of electron-impact induced bond rupture in propane-1-C^{13} by Beeck *et al.* (15) led to the conclusion that C^{12}—C^{12} bonds were broken with a frequency about 20 per cent greater than that for C^{12}—C^{13} bonds. More detailed studies by the same group [Stevenson *et al.* (209)] of the same isotope effect in the thermal cracking of propane-1-C^{13} indicated 8 per cent greater efficiency for the C^{12}—C^{12} bond rupture. Bigeleisen (23), assuming a chain mechanism, has calculated, on the basis of statistical rate theory, a theoretical upper limit of 4 per cent for this isotope effect. As indicated by Pitzer (186), however, details of the exact mechanism are not sufficiently well-known to permit a convincing theoretical treatment of the problem.

Decarboxylation of malonic acid.—Yankwich & Calvin (43, 241) studied the isotopic constitution of the carbon dioxide and acetic acid formed in the decarboxylation of malonic acid-1-C^{14}. Their results indicate that, at 150°, C^{12}—C^{12} bonds are broken with a frequency 1.12 ± 0.03 times greater than C^{12}—C^{14} bonds. More strikingly, with carboxyl-labelled bromomalonic acid, decomposed at 115°, the frequency ratio was 1.41 ± 0.08. If these ratios are attributed to differences in activation energy for rupture of the two types of bonds, differences of 96 and 250 calories for the two acids would be indicated; since these values are too large to be accounted for by the effect of mass on the carbon-carbon stretching vibration, other factors must be assumed. Bigeleisen (24) considered these results to be in sharp disagreement with statistical rate theory, from which he calculated theoretical rate ratios (300° to 400° K.) of about 1.04 for both acids.

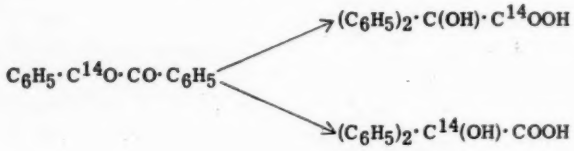
Bigeleisen & Friedman (25) investigated the decarboxylation of isotopically normal malonic acid, following the ratio of $C^{13}O_2$ to $C^{12}O_2$ produced, and found, for the type of rupture studied by Yankwich & Calvin (241), rate constant ratios for C^{12}—C^{12} rupture to C^{12}—C^{13} rupture to be 1.020 and 1.019

in two experiments; these results are to be compared with a theoretical (24) value of 1.0198.

While these data and the predictions of statistical theory are entirely inconsistent with the findings of Yankwich & Calvin on malonic acid-1-C^{14}, Pitzer (186) employs a different molecular model in calculating the theoretical rate constant ratio, and finds a value of 1.14. While this is in good agreement with the Yankwich & Calvin data on malonic acid, Pitzer finds no basis for predicting a higher value for the ratio in the bromomalonic acid case, where the experimental result is less certain. In discussing limitations of the theoretical treatment of the problem, Pitzer points out that statistical rate theory assumes a full equilibrium concentration of activated complexes; in an isotopically asymmetric molecule such as malonic acid-1-C^{14} activation energy for the C^{12}—C^{14} break is greater than that for the C^{12}—C^{12} break, and the molecule may, during the process of activation to the former, react by the C^{12}—C^{12} break, tending to deplete the concentration of C^{12}—C^{14} activated complexes below the equilibrium value. This process would lead to unexpectedly high values of reaction rate ratios. An additional factor resulting from failure of the reaction to maintain equilibrium concentrations of activated complexes might be a greater probability of C^{12}—C^{12} rupture in the normal than in the isotopic molecule, since the former contains two bonds of this type. The work of Beeck *et al.* (15) indicates that the C^{12}—C^{12} break in a $C_3H_8^+$ ion with one C^{13} is about 7 per cent more probable than in the isotopically normal species (186).

Decomposition of oxalic acid.—In experiments by Lindsay, McElcherhan & Thode (143), isotopically natural oxalic acid was decomposed in the presence of concentrated sulfuric acid, and the resulting CO and CO_2 analyzed for C^{13} mass-spectrometrically. It was found that C^{13} showed a preference for CO_2 over CO, the observed rate constant ratio for the process being 1.033. The rupture of C^{12}—C^{12} bonds was found, as expected, to be more probable than that of C^{12}—C^{13} bonds, by a factor of 1.034. The preference of C^{13} for CO_2 was believed to reflect a preferential splitting of the C^{12}—O^{16} bond over the C^{13}—O^{16} bond.

Benzilic acid rearrangement.—The rearrangement of monocarbonyl-labelled benzil may produce either benzilic acid-1-C^{14} or benzilic acid-2-C^{14}:



Distribution of C^{14} among these products was determined by Stevens & Attree (208), who performed lead tetraacetate decarboxylation and determined activity of the resulting benzophenone for comparison with that of the original benzil. The results indicated that the amount of benzilic acid-2-C^{14}

formed in the rearrangement was greater by a factor of 1.11 ± 0.01 than that of benzilic acid-1-C^{14}.

Hydrolysis of ethyl benzoate.—Stevens & Attree (207) have studied the alkaline hydrolysis of ethyl benzoate labelled with C^{14} in the carboxyl position. Measurement of the C^{14} activity in the initial and final stages of the hydrolysis indicated a ratio of rate constants for the hydrolysis of the normal and isotopically labelled compounds of $k/k^* = 1.16 \pm 0.017$.

Organic Reaction Mechanisms

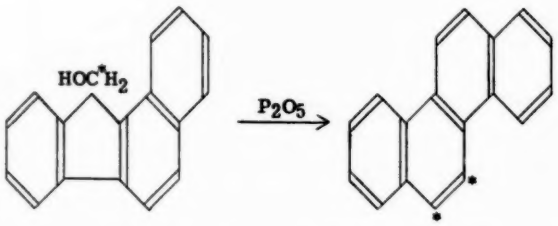
The applications of isotopic tracers, particularly those of carbon, to the study of organic reactions have multiplied rapidly in recent months, and in addition to the excellent book by Calvin *et al.* (42), several reviews of various aspects of the subject have been published. Among these is a critical treatment of organic radiochemistry by Starke (206). Arnstein & Bentley (11) have reviewed both the tracer techniques in organic chemistry and a large number of organic reaction mechanisms (12) studied isotopically. A Russian review (4) appears to be more general in nature, covering production and properties of the carbon isotopes and their applications in chemical and biochemical studies. Here we shall be restricted to those recent studies which have been directed towards elucidation of reaction mechanisms.

Rearrangements.—Wagner-Meerwein type rearrangements of *t*-butyl and *t*-amyl alcohols and chlorides have been studied by Roberts, McMahon & Hine (191), using C^{14}-tagged compounds, subsequently degraded to determine the position of the tracer atom. No significant rearrangement was observed in the nonreversible metathetical and elimination reactions. Position rearrangements occurred in *t*-amyl chloride in contact with aluminum chloride, presumably by a carbonium ion mechanism. Distribution of the C^{14} among three positions, including its original (tertiary C) position was:

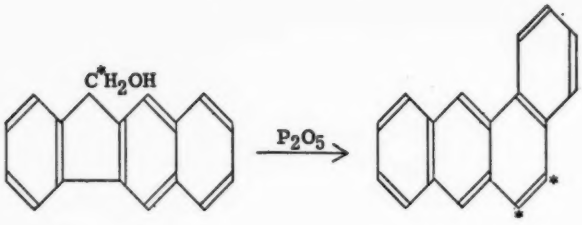
$$(CH_3)_2 \cdot C^*(Cl) \cdot CH_2 \cdot CH_3 \rightleftarrows (CH_3)_2 \cdot C(Cl) \cdot C^*H_2 \cdot CH_3 \rightleftarrows (CH_3)_2 \cdot C(Cl) \cdot CH_2 \cdot C^*H_3$$

64 per cent 35 per cent 1 per cent

Rearrangement of 1,2-benzofluorenemethanol-10-C^{14} to give chrysene-5,6-C^{14}:



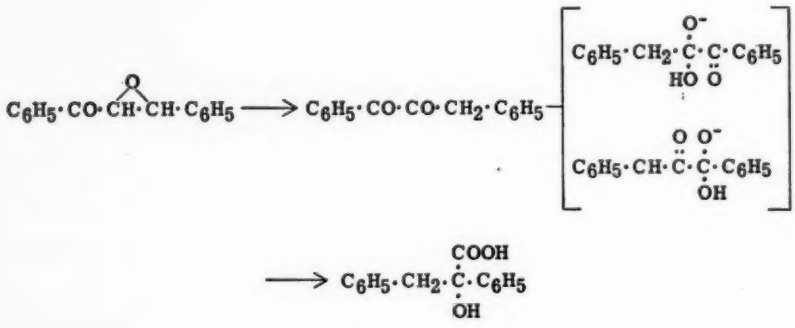
has been demonstrated by Toffel, Jones & Collins (217). Degradative studies indicated 60 per cent of the C^{14} in the 5-position, 40 per cent in the 6-position. Burr & Collins (39) similarly observed rearrangement of 2,3-benzofluorenemethanol-10-C^{14} to 1,2-benzanthracene-5,6-C^{14}:



Here 45 per cent of the C^{14} was found in the 5-position, indicating near equivalence in migration aptitudes of phenyl and β-naphthyl groups in rearrangements of this type.

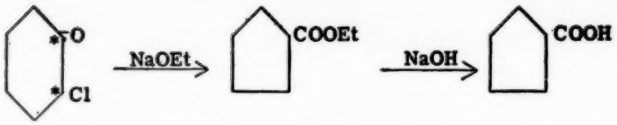
Phenylglyoxal has been converted to mandelic acid without shift in position of the ketone carbon atom in two experiments [Doering *et al.* (63); Neville (169)]. Intramolecular transfer of the hydrogen atom was indicated (63) by failure of solvent deuterium to become attached to the alcohol carbon atom of mandelic acid in this alkali-catalyzed conversion.

A study of the benzylideneacetophenone oxide rearrangement (in alcoholic alkali) to α-hydroxy-α,β-diphenylpropionic acid has been made by Collins & Neville (48). The process is believed to occur by means of a benzylic-acid type rearrangement of the known intermediate benzyl phenyl diketone, so that the over-all process may be illustrated as:



It is apparent that two possible ionic intermediates can participate in the process, one involving migration of a phenyl group, the other of a benzyl group. Degradative studies of the product have excluded phenyl group migration, giving results consistent with benzyl group migration. A summary of published (170) and unpublished results of the studies of unsymmetrical α-diketone ($R \cdot CO \cdot CO \cdot R'$) rearrangements is presented in Table I [Neville *et al.* (171)].

The mechanism of the Faworskii rearrangement has been investigated by Loftfield (145), employing chlorocyclohexanone, which is converted by alkali to cyclopentane carboxylic acid:



Degradation of the product showed 52 per cent of the C^{14} in the carboxyl position, and the remaining 48 per cent distributed equally between the α and β ring positions. Exchange between these two positions has not been eliminated, but the results suggest a path through cyclopropanone or some other intermediate in which the 2- and 6-positions of the chlorocyclohexanone are equivalent.

TABLE I

R	R′	Migration R	Migration R′
		per cent	*per cent*
phenyl	hydrogen (63, 169)	0	100
methyl	carbethoxy	0	100
phenyl	benzyl (48)	0	100
phenyl	*p*-methoxyphenyl (170)	68.5	31.5
phenyl	*p*-methyl phenyl	61.8	38.2
phenyl	*p*-chlorophenyl (170)	38.8	61.2
phenyl	*m*-chlorophenyl	18.9	81.1

Studies of the decarbonylation of diphenyl triketone by Roberts, Smith & Lee (192) have demonstrated that the center carbonyl group exclusively is lost if the reaction is induced by aluminum chloride, cupric acetate, or sodium hydroxide. This result implies that a 1,2-shift of a benzoyl group is highly favored over that of a phenyl group in this reaction. The same investigators report that the cupric acetate-induced decarbonylation of *p*-methoxyphenyl phenyl triketone proceeds in a similar manner, and that the benzilic acid-type rearrangement of *p*-methoxybenzil shows preferential migration of the phenyl group.

Displacement reactions.—A summary of recent studies of mechanisms of displacement reactions is given by Hughes (105). Studies of isotopic exchange, particularly between halide ions and organic halides, have given valuable information on these mechanisms, and a detailed discussion of solution substitution reactions involving heterolytic bond fission was held at the Paris symposium on isotope exchange (49) in 1948. Exchange of hydrogen ions with unsaturated aliphatic compounds has been shown (49) to proceed by either bimolecular or unimolecular mechanisms of electrophilic substitution (S_E2 or S_E1) and a bimolecular mechanism involving rearrangement (S_E2') is apparently also possible. In halogen exchange, nucleophilic mechanisms (S_N1 or S_N2) are supported (70), with no evidence for an efficient S_N2' mechanism (105). The S_N2 mechanism is believed (105) to lead generally to

inversion of configuration. Thus prototropic systems can apparently exchange hydrogen ions with rearrangement, while anionotropic systems are disinclined to rearrange while exchanging anions. This lack of correspondence between the two types of mechanisms is considered (104) to be highly significant, perhaps reflecting the same fundamental structural differences responsible for the dissimilarities between the reactions of aliphatic and aromatic compounds. With saturated compounds (or in saturated groups) where only σ electrons are present, nucleophilic processes predominate. The π electrons of unsaturated carbon atoms, however, are so directed as to decrease the probability of nucleophilic attack and as to be geometrically vulnerable to electrophilic attack.

Melander (157, 158) has described a thorough investigation of the mechanism of electrophilic aromatic substitution, employing the isotope effect on reaction rates in a unique manner. Substitution reactions may proceed either by a straightforward one-step S_E2 mechanism, or by a two-step mechanism involving a quinonoid intermediate. Theoretical considerations predict quite different effects of substituting tritium for ring-attached protium in the two mechanisms. Provided the first step of the two-step mechanism is rate-determining no isotope effect should be observed, while a significant difference in rate between tritium and protium positions should be observed in the pure S_E2 mechanism or in the two-step process with the second step rate-determining. Reactions occurring by the two-step process with the first step rate-controlling were nitration of benzene, *m*-nitration of nitrobenzene, *o*-nitration of toluene and bromobenzene, *o*-nitration of *p*-nitrobromobenzene, α-nitration of naphthalene, and probably *o*-nitration of *p*-nitrotoluene. Bromination of benzene and bromobenzene in the presence of various catalysts gave obscure results because of exchange of hydrogen between liberated hydrogen bromide and the aromatic nucleus; this exchange was slowest with iodine catalysis, where the results indicated the same mechanism as for nitration. Sulfonations of benzene and bromobenzene apparently proceed by either the pure S_E2 process, or have a second step which is rate-controlling.

Miller & Willard (159) have studied the kinetics of a simple thermal displacement reaction, that of bromine with carbon tetrachloride, which proceeds at convenient rates between 180° and 250°. The initial rate was found to be proportional to the square root of bromine pressure. Acceleration of the reaction by added chlorine is attributed to an increased production of free radicals by the reaction:

$$Cl + CCl_4 \rightarrow Cl_2 + CCl_3,$$

which is favored energetically over the corresponding reaction with bromine atoms. The activation energy for free radical production was estimated to be 18 kcal. per mole for bromine and 12 kcal. per mole for chlorine.

Oxidation reactions.—Products of the alkaline permanganate oxidation of propionate-1-C^{14} have been examined by Mahler & Roberts (151). In the presence of a large alkali excess the ratio of α-C to carboxyl-C rupture was about nine to one, agreeing with earlier studies (166) with C^{11}, and placing

the isotope effect within the limits of experimental precision. Oxidation of pyruvate-2-C^{14} by hot alkaline permanganate gave 80 per cent transformation to tagged oxalate and inactive carbonate; the remaining 20 per cent yielded labelled acetate and inactive carbonate. If pyruvate is an intermediate in propionate oxidation, a pathway through decarboxylation must thus be considered as part of the mechanism.

The heterogeneous oxidation of acetylene over silver nitrate has been studied by Johnson & Krieger (112) using C^{14} as tracer. Acetylene at a concentration of 5 to 10 p.p.m. in air was passed over silver nitrate supported on a high or a low specific surface alumina at 149°, and the amount of acetylene removed (by adsorption or by oxidation) determined from activity measurements. The catalytic activity was found to be a function of silver nitrate concentration in the support, reaching a maximum at about 10 per cent silver. The appearance of catalytic activity corresponded closely with the appearance of crystalline silver nitrate and some metallic silver was produced in the process. Dependence on the surface area of the support was not simple. Products of the oxidation included CO_2 and either carbon or some high molecular weight carbon compound which remained with the catalyst; no carbon monoxide was detected.

Hydrolysis.—Exchange of O^{18} in the carbonyl position of ethyl benzoate, isopropyl benzoate, and *t*-butyl benzoate with the solvent oxygen during hydrolysis has been demonstrated by Bender (16). The results suggest a true intermediate, in which the carbonyl oxygen participates, in a reversible manner, in the hydrolysis. Since the intermediate must assume a symmetrical structure, the unionized hydrate of the ester may be involved. Rate-constant ratios for the hydrolysis and exchange reactions in 33 per cent dioxane solution were found to be $k_h/k_e = 11$ for ethyl benzoate and $k_h/k_e = 7$ for *t*-butyl benzoate. Similarity of intermediates in all cases is suggested by similarity in the ratios, and by near equality of the ratios for alkaline and acid hydrolysis of ethyl benzoate. Variations in the ratio with changes in the alkoxyl radical and in the dielectric properties of the solvent are explained on the basis of relative ease of breakage of the C—OR bond and the C—OH bond in the intermediate.

Similar studies by Long & Friedman (147) of the mechanism of the γ-butyrolactone hydrolysis, carried out in H_2O^{18} by the action of either 3 *M* sodium hydroxide or 0.8 *M* sulfuric acid and followed by reformation of the lactone from the products, have indicated that both the acid-catalyzed and basic hydrolyses proceed by means of an acyl-oxygen bond split.

The cuprous chloride-catalyzed hydrolysis of *cis*- and *trans*-1,3-dichloropropene has been studied by Tweedie *et al.* (220). In an effort to determine relative rates of hydrolysis in the two Cl positions, the material was prepared with Cl^{36} in the allylic position ($CHCl=CH-CH_2Cl^*$). With both geometrical isomers, removal of the radioactive chlorine was much more rapid than that of the inactive chlorine in the vinylic position.

Catalysis.—A critical discussion of the use of isotopic tracers in catalytic research was presented by Turkevich (218) at the Brookhaven conference on

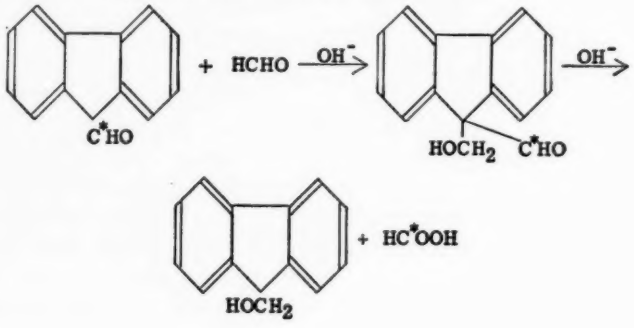
isotope exchange. Catalytic reactions on iron catalysts have been studied by Kummer, DeWitt & Emmett (133), in connection with a general analysis of the mechanism of the Fischer-Tropsch synthesis. With a surface layer of iron carbide-C^{14} on the catalyst, only a small fraction of the product hydrocarbon mixture was tagged; with labelled CO, very little of the label remained with the catalyst. Thus the process is not believed to proceed normally through a surface carbide intermediate. Preliminary studies of the adsorption of $C^{14}O$ on iron catalysts, the $N^{14}N^{14}/N^{15}N^{15}$ exchange rate, and the deuterium-hydrogen reaction over iron are also described (134).

Karpacheva & Rozen (122) conclude from O^{18} tracer studies that very few catalysts act by purely adsorptive processes without formation of intermediate species. Their studies, all with O^{18}-labelled catalysts, included oxidation of hydrogen on various oxides, oxidation of carbon monoxide on manganese dioxide, and dehydration of alcohol on kaolin and on a mixture of chromic oxide and alumina.

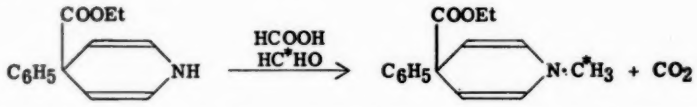
Catalytic polymerization of organic cations and anions has been studied by Landler (136). Styrolene polymerized to a mean molecular weight of 46000 over bromine-tagged stannic bromide contained about one molecule of catalyst to every three of polymer, while methyl methacrylate produced by Grignard catalysis to a mean molecular weight of 20000 contained somewhat more than one Grignard reagent molecule for every two of the polymer.

Other carbon-traced reactions.—Willgerodt reaction: Acetophenone labelled in the carbonyl position with C^{14} was converted to phenylacetamide by the action of yellow ammonium sulfide in experiments by Dauben *et al.* (53, 54). Hofmann degradation of the product yielded nearly inactive carbon dioxide, indicating a nonrearrangement mechanism for the major pa hway of the reaction. Phenylacetic acid produced as a minor product in the reaction, however, yielded carbon dioxide of specific activity about 75 per cent that of the starting material, so that it must arise, at least in part, through a molecular rearrangement.

Reaction of formylfluorene with formaldehyde: The reaction of 9-formylfluorene-10-C^{14} with aqueous formaldehyde is reported by Burr (38) to yield nonradioactive 9-fluorenemethanol, and the C^{14} was found quantitatively in formate ion. The suggested mechanism is illustrated:



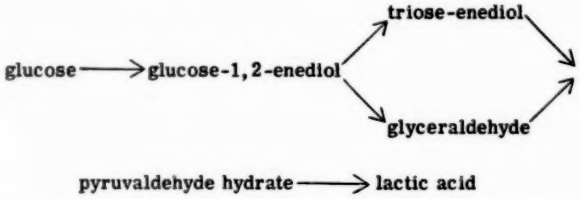
Formaldehyde-formate reductive methylation: In the preparation of demerol (N-methyl-4-phenyl-4-carbethoxypiperidine hydrochloride), Tarpey *et al.* (212) have clarified the roles of formaldehyde and formic acid in the reductive methylation:



With C^{14} in the formaldehyde the carbon dioxide produced was inactive, while the product was equal in specific activity to the original formaldehyde. With the label in the formic acid, however, no activity appeared in formaldehyde or demerol, and the CO_2 produced had the expected activity. The results indicate that formaldehyde supplies the methyl group, that formic acid is the reducing agent, and that no C^{14} exchange occurs between formaldehyde and formic acid under conditions of the run.

Epimerization of glucose: Bothner-By & Gibbs (30) have reported that no skeletal rearrangement of carbon atoms occurs in the epimerization of glucose-1-C^{14} in alkaline solution.

Formation of lactic acid from glucose: Studies by Gibbs (80) of the conversion of glucose to lactic acid in alkaline solution, with glucose-1-C^{14} and glucose-3,4-C^{14} have indicated the mechanism:



Decomposition of acetyl peroxide: Preliminary studies of the decomposition of acetyl peroxide in acetic acid-2-C^{14} by Fry *et al.* (77) confirm in a general way a mechanism already proposed by Kharasch & Gladstone (123), in which the reaction products are succinic acid, methane, carbon dioxide, and some methyl acetate. The observed appearance of activity in the methyl acetate is, however, not explained by the previously proposed mechanism, but could perhaps be accounted for on the basis of exchange reactions between acetic acid and free methyl or acetate radicals. No appreciable exchange was observed between acetic acid and diacetyl peroxide under conditions of the reaction, or between methyl acetate and acetic acid at 100° for five hours.

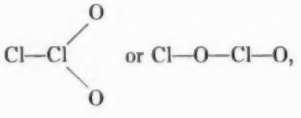
Halogen-traced reactions.—The utilization of radioactive halogens in identification of free radicals has been described by Durham, Martin & Sutton (67) and by Williams & Hamill (235). Systems in which the free radicals were produced were spiked with molecular radiohalogens, so that the correspond-

ing halides were formed. These were then separated by fractional distillation with added carriers, and subjected to radioassay. Durham *et al.* demonstrated that the action of sodium on propyl bromide produced only propyl radicals at ordinary temperatures, but produced methyl radicals in addition at 400°, with an activation energy of about 19 kcal. per mole. The photodecomposition of methyl ethyl ketone at a wavelength of 2532 Å produced 2.5 times as much ethyl as methyl, while at 3100 Å the ratio was considerably greater. Williams & Hamill applied their technique to a study of gamma-radiolysis of *n*-pentane, employing I^{131} in solution as iodine. Activity was found in a variety of lower alkyl iodides. Photobromination of *n*-pentane at 80° produced lower bromides in a 30–70 ratio to amyl bromides over a wide range of bromine-pentane pressure ratios.

Inorganic Reaction Mechanisms

Exclusive of isotopic exchange processes relatively few inorganic reactions have been subjected to critical isotopic tracer studies designed to elucidate their mechanisms. A general discussion of inorganic mechanisms as related to rate studies has been presented by Forbes (72), employing data from the rate-constant tables to be published soon by the National Bureau of Standards, under the editorship of N. Thon. It is hoped that the studies described below will illustrate the applicability of tracers to the clarification of mechanisms.

Oxidation-reduction reactions of chlorine.—One of the most thorough mechanism studies, including a discussion of earlier work, is described by Taube & Dodgen (213), who employed Cl^{38} to study the phenomena accompanying changes in the oxidation state of chlorine. Specifically studied were the oxidation of chlorite by chlorate, the reaction of chlorite with chlorine and with hypochlorite, the reduction of chlorate to the dioxide by chloride, and the disproportionation of chlorite in acid. Principal points indicated by the results were: (*a*) the oxidation of chlorite by chlorate in acid is much slower than the disproportionation of chlorite; (*b*) in the oxidation of chlorite to chlorine dioxide or to chlorate by chlorine or by hypochlorite, most of the chlorine atoms in the product species are derived from the chlorite; (*c*) in the reaction $4H^+ + 2Cl^- + 2ClO_3^- = Cl_2 + 2ClO_2 + 2H_2O$, the chlorine atoms in the dioxide are derived largely from the chlorate; (*d*) in the disproportionation of chlorite in acid ($4HClO_2 = Cl^- + 2ClO_2 + ClO_3^- + 2H^+ + H_2O$), catalyzed by chloride ion, the chlorine atoms in the dioxide are largely derived from the chlorite. Arguments are presented for an unsymmetrical intermediate,



or Cl—O—Cl—O,

in systems (*b*), (*c*), and (*d*).

Oxygen atom transfer.—The transfer of oxygen atoms (O^{18}) in oxidation-reduction reactions in aqueous systems (e.g. chlorate-sulfite) has been studied by Taube *et al.* (41, 95), in an effort to distinguish between two mechanisms: (*a*) the direct transfer of an oxygen atom, and (*b*) the formation of an intermediate capable of deriving oxygen atoms from the solvent. For the chlorite-sulfate case these may be illustrated as:

(*a*)
$$SO_3^{=} + ClO_3^{*-} \xrightarrow{(+H^+)} SO_3O^{*=} + ClO_2^{*-}$$
$$SO_3^{=} + ClO_2^{*} \longrightarrow \text{etc.}$$

(*b*)
$$SO_3^{=} + ClO_3^{*-} \xrightarrow{(+H^+)} O_3S{:}ClO_2^{*-}\ (+OH^-)$$
$$H_2O + O_3S{:}ClO_2^{*} \longrightarrow SO_4^{=} + 2H^+ + ClO_2^{*-}.$$

Results indicate that two of the three atoms lost by ClO_3^- in reduction to Cl^- appear in the product sulfate, indicating a direct transfer mechanism. The last stage of the process, reduction of hypochlorite to chloride, probably loses one tracer oxygen atom to the solvent by exchange, perhaps through the chlorine hydrolysis equilibrium.

The reaction between sulfur dichloride and sulfur trioxide has been studied by Muxart *et al.* (163), using S^{35} as tracer. With the label on the dichloride initially, 80 to 90 per cent of it appears in thionyl chloride, according to the scheme:

$$S^*Cl_2 + SO_3 \rightarrow SO_2 + S^*OCl_2,$$

indicating a direct oxygen atom transfer. It is proposed that the remainder of the tracer arrives in SO_2 by a reaction in which oxygen from the trioxide displaces chlorine in the dichloride.

Decomposition of ammonium nitrate.—The thermal decomposition of ammonium nitrate:

$$NH_4NO_3 \rightarrow N_2O + 2H_2O$$

has been studied by tracing nitrogen from $N^{15}H_4NO_3$. Kummer (132) found essentially only $N^{15}NO$ as product, indicating bond formation between the ammonium and nitrate nitrogen atoms. Additional studies of the same system by Friedman & Bigeleisen (75) lead them to exclude oxidation-reduction mechanisms whereby the two nitrogen atoms arrive at the same chemical form (e.g. NOH), and to propose a dehydration mechanism:

$$NH_4^+—NO_3^- \rightarrow HN{=}NO_2^- + H^+ \rightleftarrows HN{=}N\begin{matrix}O\\ \diagdown\\ \diagup\\ OH\end{matrix}$$

$$H—N{=}N\begin{matrix}O\\ \diagup\\ \diagdown\\ OH\end{matrix} \rightarrow N_2O + H_2O.$$

Diffusion

Descriptions of procedures, together with relevant equations, for determining diffusion coefficients with tracers, are presented (for liquids) by Anderson & Saddington (8), and (for solids) by Lindner (142), and Zimens *et al.* (243). An interesting sign of the times is the title of a paper by Kuczynski (131), "Measurement of the Self-Diffusion of Silver without Radioactive Tracers."

A study of the differential diffusion coefficients of sodium ion in sodium chloride solution has been made by Adamson *et al.* (2), employing 3-year Na^{22} and 14.8-hr. Na^{24}. No effect of isotopic mass on diffusion behavior was observed. Their results, obtained by the glass diaphragm technique, disagreed sharply with the diffusion coefficients predicted from the limiting law equation for values at 25° and 35°. Investigation revealed that a systematic error arose from surface diffusion of ions adsorbed on the walls of the diaphragm pores. The authors conclude that the validity of diffusion coefficient values obtained for dilute solutions with the glass diaphragm technique is questionable. However, Whiteway *et al.* (230) find by the same technique good agreement between experiment and the limiting law prediction for silver ion diffusion, employing the 225-day Ag^{110}.

A new type of diffusion cell, together with the technique and theory of tracer diffusion measurements, is described by Wang & Kennedy (227). The procedure was applied to the determination of the self-diffusion coefficients of sodium ion (Na^{22}) and iodide ion (I^{131}) in aqueous sodium iodide solutions (10^{-4} to 3.5 *M* at 25°). Results indicated, for iodide ion, $D° = 2.035 \times 10^{-5}$ sq. cm. per sec., compared with a theoretical value of 1.34×10^{-5} sq. cm. per sec., a difference of 7 per cent. This experimental value agrees within 0.7 per cent with that obtained by Adamson (1) by the glass diaphragm technique.

Measurements of self-diffusion of tungstate species in 0.0025 to 0.05 *M* sodium tungstate solutions, pH 2.3 to 11.3, have been made by Anderson & Saddington (8), using the 24-hr. W^{187}. The diffusion constant was essentially independent of pH above pH 9 and below pH 5, showing values of $D = 7.7 \times 10^{-6}$ sq. cm. per sec. and $D = 3.47 \times 10^{-6}$ sq. cm. per sec., respectively. A steady decrease was observed between pH 9 and 5. The results are interpreted in terms of reversible equilibria between polyacid anions of tungsten, largely uncondensed WO_4^{-} in alkali, possibly hexa- or heptatungstate in acid.

A discussion of the theory of self-diffusion of ions in ionic crystals is presented, along with data on the diffusion of sodium in sodium chloride and sodium bromide, by Mapother, Crooks, & Maurer (152). Accepted theory postulates migration of Schottky vacancies, as they become occupied by neighboring ions, for the diffusion mechanism. The theoretical ratio of crystal conductivity σ to self-diffusion coefficient D for an alkali halide is given by the Einstein relation:

$$\sigma/D = Ne^2/kT,$$

where N is the number of alkali ions per unit volume of crystal. Measure-

ments of self-diffusion (Na^{24}) and conductivity in sodium chloride and sodium bromide crystals indicated that this relationship is satisfied at high, but not at low, temperatures. Dependence of the diffusion coefficients on temperature followed the Schottky-Wagner vacancy theory if account was taken of ionic impurities.

Utilizing as an indication of diffusion extent the low penetrating power of beta-particles from Ag^{111} and Hg^{203}, Zimens *et al.* (243) obtained diffusion coefficients of silver and mercury in Ag_2HgI_4 crystals as a function of temperature. The values for silver agreed with those calculated from electrical conductivity.

Preliminary measurements by Lindner (142) indicate good agreement between the experimental and calculated values of D for silver sulfate between 250° and 650°. Constants between 10^{-14} and 10^{-12} sq. cm. per sec. were obtained for lead oxide between 485° and 570°. Zinc was found to diffuse more rapidly in zinc-iron spinel than in pure zinc oxide. Diffusion of calcium in the system $CaO\text{-}SiO_2$ was observed to be quite slow.

In isotopic exchange studies, the coefficient of self-diffusion of sulfur in monoclinic sulfur was determined by Haissinsky & Peschanski (93) to be 1.83×10^{-14}, 3.80×10^{-14}, and 10.72×10^{-14} sq. cm. per sec., respectively, for 103°, 108°, and 115°. The extrapolated value for 18° was 2.83×10^{-22} sq. cm. per sec.

Surface diffusion of radioactive silver on silver metal has been examined by Nickerson & Parker (174), who report diffusivities at 10^{-6} mm. Hg of 0.018, 0.03, and 0.147 sq. cm. per hr. at 225°, 250°, and 350°, respectively, indicating an activation energy of about 10.3 kcal. per gm. atom.

Surface Phenomena

Thorough reviews of radiochemical colloidal and surface phenomena are presented by Broda (31) and by Wahl & Bonner (224), so that only the most recent developments need be described here.

A significant contribution to the field of tracer surface chemistry has been made by Frauenfelder (73), who describes apparatus and techniques for the determination of desorption probabilities, sticking coefficients, and surface diffusion coefficients, employing recoil atoms from K-capture processes as indicators. Relevant equations are developed, and a comparison of results from these techniques with those from more conventional ones is given.

The "emanation method" of Hahn, which has had several familiar applications, is described in detail in a recent paper (86). Incorporation of a radionuclide with a gaseous daughter into a solid and subsequent measurement of the rate of gas release may give information on surface area, inner surface, deformations, and solid-state reactions of the solid. Dependence of the emanation rate on ageing, humidity, temperature of precipitation, and heating is described for a variety of types of solid materials.

A review by Paneth (181) of the exchange of ions between solutions and crystal surfaces discusses application of this technique to determination of

specific surface of the solid material. Application of the procedure to strontium sulfate precipitates by Stow & Spinks (210), using Sr^{90} and S^{35} led to rather unsatisfactory results; strontium ion exchange indicated a specific surface of 1.5 m.²/gm., while sulfate ion exchange indicated 0.83 m.²/gm. for the same precipitate, formed from a solution containing an excess of sulfate ion. This discrepancy may be a function of mode of precipitation, lack of precision in selection of ionic radii, or, perhaps, differences between surface activity coefficients for the anion and the cation.

The perennial studies of radium coseparation phenomena by Khlopin *et al.* continue. Surface tension-lowering substance in solution are said (125) seriously to suppress the efficiency of coprecipitation of radium with isomorphous solids, such as lead sulfate. Studies (124) of the lanthanum fluoride-radium fluoride system at 100° confirmed the authors' prediction that the distribution coefficient for such a system (mixed-valency "isomorphism") would vary widely with concentration of the microcomponent.

Lindberg & Hummel (141) discuss paper chromatography of radioelements. Adsorption of 10.6-hr. Pb^{212} (ThB) and 19.5-day Rb^{86} on paper as a function of pH has been measured by Broda & Schönfeld (34), who conclude that the phenomenon proceeds by an ion exchange mechanism. If only free carboxyl groups of cellulose are involved, the results indicate one carboxyl group for about 125 glucose units in cellulose.

Application of ion-exchange resins to isolation and purification of radioelements has made rapid strides in recent months. Cation exchangers have been successfully applied to the separation of zirconium and hafnium (17). Adsorption of iron (161) and protoactinium (130) from hydrochloric acid solutions by anion exchangers has been demonstrated, and anion resins have been used for separations of zirconium and hafnium (129), zirconium and niobium (223), and the anions of periodic group VII(13).

A general discussion of radiocolloid formation is given by Broda & Erber (33), who also describe the radiocolloidal behavior of manganese dioxide formed by neutron-irradiation of potassium permanganate. Broda & Epstein (32) describe the use of concentrated photographic emulsions (80 per cent AgBr) to study radiocolloid formation in very dilute solutions of polonium. Differences in behavior of cations and radiocolloids of zirconium and niobium toward cation exchange resins are described by Schubert & Richter (199), who determined distribution coefficients of these elements between radiocolloidal solutions and a cation resin. Behavior of radiocolloids of thorium (UX_1) at concentrations about 10^{-15} M in aqueous solution has been studied by Kurbatov *et al.* (135). The fraction of tracer removed by filtration was a direct linear function of pH between pH 1 and pH 4.5, consistent with results of similar studies on yttrium and zirconium. Small amounts of carbonate ion, probably due to complex ion formation, markedly decreased the extent of radiocolloid formation.

The use of radioactive tracers to determine adsorption of solutes on liquid surfaces has been applied by Aniansson & Lamm (9) and by Judson *et al.*

(117). Aniansson (9) describes the theory and procedure of the method, involving direct counting of weak beta particles (e.g., S^{35}, Ca^{45}) from the solution surface. Results of measurements on hexadecyl sodium sulfate and calcium ion as impurities in dodecyl sodium sulfate solution (9) and an adsorption isotherm for di-*n*-octyl sodium sulfosuccinate (Aerosol OTN) (117) are presented. Extension of the method to liquid-solid and liquid-liquid interfaces is proposed (9).

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ANALYTICAL NUCLEAR CHEMISTRY

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The application of radiochemical methods to chemical analysis has increased considerably from the original work of Hevesy & Hobbie (84) who determined the lead in rocks by a tracer technique. Since that time and especially since 1945 there has been a growing interest in radiochemical methods of chemical analysis. The increase, however, in this latter period has not been as great as one would think. No doubt more use would be made of these methods if it were not that a certain reluctance to enter this work by chemists has been caused by the uncertainty as to handling radioisotopes, the need of expensive, temperamental instruments for measurements, and the lack of training in the necessary techniques.

The cost of the isotopes themselves in some instances is no small matter. In the past few years a considerable number of publications have done much to remove the mystery which, to many chemists, surrounded the use of radioisotopes. Many companies are now supplying service as well as instruments so that an electronics man is not needed.

The present review will be an attempt to collect the work of the past two or three years in the field of radiochemistry for chemists who are interested in analysis. At the risk of repeating other work in this series, some consideration will be given to the instruments and equipment used in addition to specific applications.

The extreme sensitivity and speed of radiochemical methods, with an accuracy ranging from fair to good, make their application to biochemical and organic analysis of considerable importance and it is in these fields that they have found most use. The application to inorganic analysis has been limited. The techniques employed have resolved methods in more or less of a pattern as follows: (*a*) analysis of naturally occurring radioactive elements, (*b*) isotope dilution analysis, (*c*) activity analysis, (*d*) activation analysis, and (*e*) neutron absorption analysis.

Of the above, the use as applied to naturally occurring radioactive elements is obvious. Concerning isotope dilution methods, it may frequently occur that quantitative analysis for a component of a mixture is wanted where no quantitative isolation procedure is known. Particularly from a complex organic mixture it may be possible to isolate from the unknown the desired compound with satisfactory purity, but only in low and uncertain yield. If to the unknown a certain activity of tagged molecules of the element in question is added, then, when the desired compound is recovered, the amount lost in the procedure can be determined by measuring the amount of tagged atoms which are recovered by radiochemical means. Activity analysis is defined as the identification and determination of the radioactivity

of individual constituents in a mixture of radioactive materials. In activation techniques the unknown sample is subjected to activation by neutrons, deuterons, or other radiation, and the radioactive chemical elements formed are analyzed and identified by their decay properties in conjunction with ordinary chemical processes.

A fundamentally different method is the measurement of the absorption of slow neutrons in a sample by certain elements. This property can be used to determine these elements.

General

The chemist who is using radioactive tracers is usually interested first in the selection of a suitable tracer, followed by the procurement of the chosen radioactive sample, and, then, the synthesis of the tracer substance incorporating the radioactive atoms. After this he has to perform the necessary chemical operations and measure the activity.

Paneth (130) has reviewed the selection and preparation of radioactive tracers. Radioactive hazards, the operation and construction of a radiochemical laboratory, and the precautions necessary have been discussed in a book by Schweitzer & Whitney (153). The excellent book by Friedlander & Kennedy (62) is presumably meant as a textbook for a radiochemical course and gives much useful information on instruments, techniques, tracers, tables of energies, and half lives, and has some applications to analytical chemistry. The National Bureau of Standards' circular (125) gives experimental values of half lives, radiation energies, isotopic abundance, and cross sections which are very useful in choosing the tracer desired and is also useful in activation analysis. A comprehensive Handbook of Radioactivity and Tracer Methodology covering nucleii and radioactivity, the measurement of radioisotopes, and biological and medical applications of radioisotopes, which has an excellent bibliography on inorganic as well as organic elements, has been compiled by Siri and his co-workers (158). The compilation by Goodman (67) has considerable material of general interest.

For those biochemists and biologists who formerly had to make long and tedious separations before chemical analysis could be made, the advent of C^{14} is of the utmost importance. The books by Kamen (94), Hevesy (82), Calvin *et al.* (23) and the review articles by Miller & Price (120, 121) and Aĭvazov *et al.* (3) have much information on the preparation, use, and assay of this and other tracers and, in many instances, eliminate the necessity for gathering data from scattered sources.

The procurement of radioactive isotopes is a relatively simple matter and has been discussed by Aebersold (1). A list of available isotopes at Oak Ridge, with the cost, can be obtained from the Isotopes Branch of the U. S. Atomic Energy Commission, Oak Ridge, Tennessee (181). Consideration must be given to undesirable radioactive impurities which may be present in tracers. Methods of removal of these impurities by precipitation, ion exchange, solvent extraction, and volatilization are given by Cohn (26).

The safe handling of radioisotopes (180) is important. In general, the analyst will be working with microcurie and millicurie levels of radiation, and with proper equipment and precautions, tracers are no more difficult to work with than other chemicals. Manov & Lintz (116) describe the different types of radiation with permissible exposure and various monitoring devices, while Failla (51) gives precautions for personnel protection.

The level of the radiation to be used will determine to a large extent the cost of laboratory furniture. The importance of radioactivity on the design of chemical laboratories has been discussed by Tompkins & Levy (175) and Ray (138, 139). For setting up a small laboratory for general purpose work, Preuss & Watson (136) give details on construction materials and instrumentation for a laboratory for radioactive organic compounds. Rice (141) has described a laboratory for use of one mc. or less, in which experimental operations at different levels of activity are separated. In his article, construction materials have been chosen for durability, stability toward solvent action, ease of cleaning, and ease and cheapness for replacement. Hoods are an important part of a radiochemical laboratory and a description of an easily constructed one of stainless steel is given by Garen & Hlad (63). Other types of hoods are described by FitzPatrick *et al.* (56) and Solomon & Foster (161).

Other laboratory equipment for various operations has been developed. Pipettes are of interest since under no condition is it advisable to use the mouth for filling. Various types have been described (10, 22, 69, 163, 178). An apparatus in which filtration, extraction, refluxing, distilling, and drying can be done has been reported by Dubbs (41) for use with biological material. Apparatus employing the advantage of the Gooch crucible have been described by Sacks (151) while Pinajian & Cross (133) have made a modified sintered glass filtering disc on which the precipitate is filtered, washed, dried, and then counted. For general equipment of all types the listing by *Nucleonics* (129) is of great use. The problem of decontamination of laboratory surfaces has been considered by Tompkins *et al.* for glass, stainless steel, and lead (173), as well as paints, plastics, and floor materials (174).

The chemist could look upon the equipment for radiochemical methods of measurements as that which, in time, will become standard laboratory equipment in much the same way as have spectrophotometers for the measurement of light absorption. In so far as the measurement of radioactivity is concerned, the analytical chemist rarely has to determine absolute quantities, since relative quantities are all that is necessary in most cases. Some short cuts can be taken in regard to measurements. The Geiger-Müller counter is the measuring device most frequently used since tracers emitting beta and gamma radiation are chiefly used at present. An excellent description of the Geiger-Müller counter in a compact package has been presented by Curtiss (33). For the measurements of radioactivity, several articles describe methods for absolute measurements (34, 35). Most methods at present employ solid samples for counting, but Freedman & Hume (60) have

suggested that liquid samples be counted since only relative values are necessary. They obtained a precision of 0.3 per cent compared to 1 per cent with solids. They also discussed the question of dipping counters versus end-window counters and were greatly in favor of the end-window counter. Their investigations showed that many commercial Geiger-Müller counters were unsatisfactory for precise analytical work. It is essential that standards be used since considerable variation between laboratories on measurements can be expected as was reported by Feitelberg (52).

Concerning instruments for use in radioactivity, a review of various types employed has been given by Borkowski (13). Two excellent reviews on techniques in radiochemical assay by Cook & Duncan (28) and Kohman (101) discuss errors which arise in beta counting from back-scattering, positioning of samples, thickness of materials, absorption, and errors in immersion counters. As mentioned above, some of these difficulties can be avoided when relative values only are desired. Several other articles on the measurement of radioactivity (8, 114, 187) as well as equipment (143, 166, 167) are of general interest. Though relatively few alpha emitters are used in tracer work, several occur in nature and are used for the determination of radium and thorium (144). Improved techniques for precision alpha radiometric assay were given by Westrum (184). In considering alpha counting mention should be made of the new scintillation counters (93) which Kuper (103), in his report on desirable improvements in nucleonic instrumentation, believes will increase in importance. Libby (108) has pointed out that many of the useful long-lived beta radiometric isotopes have soft beta radiation. The absorption of these weak radiations are discussed and relationships are developed for the treatment of the problems of absorption and intensities of radiation from sample layers of various thicknesses. The relative sensitivities of various counters are discussed; in particular, the end-window type, the screen-wall type, and the gas counter are described.

The importance of C^{14} is noted in the number of articles on the design and construction of counters for this purpose. In one, a windowless flow-type proportional counter is described (143), while another describes a windowless flow-type Geiger-Müller counter (97). Eidinoff (46) used Geiger tubes with gas pressure of 2 to 12 cm. mercury. Brownell & Lockhart (21) discuss the problems encountered in the use of carbon dioxide counters in sufficient detail to be of help to laboratories planning to use this method. Mann & Parkinson (115) have described a counter unit and external quenching circuit for use with carbon dioxide and carbon disulfide mixtures.

In connection with Geiger-Müller counters for liquids, Harris (80) uses a thin-wall counter which fits into a cup and requires only 1 to 2 ml. of liquid. Schweitzer (152) prefers the enclosed solution method when dealing with liquids. He maintains that the dipping counter method is the least efficient while the open solution counting detects the lowest energy particles. In connection with different factors influencing radiochemical work, Kelly *et al.* (96) have indicated that self-absorption, volatilization, and deliquescence

offer special problems. In working with very low concentrations, the well-known phenomenon of adsorption on various materials has been shown to occur with radioactive tracers (123). An unusual difficulty associated with handling barium carbonate containing C^{14} is reported by Claycomb *et al.* (25) where difficulty was experienced in weighing because of electrostatic charges on the sample and equipment. Using an automatic sample changer Pannell (131) has made radioassays on ores containing as little as 0.02 per cent uranium oxide. An interesting technique has been given by Lindberg & Hummel (109) for the measurement of radioactivity from paper chromatograms.

In writing a review of this type there is always the problem of where to put certain articles which cover a considerable portion of the field. The following are of such a nature. Boyd & Hume (16) have discussed the question of radiochemical analytical methods and have covered the methods of measurements, counting techniques, and the use of radioactive isotopes as applied to analytical chemistry. Consideration has been given to their use in shortening the analysis time required for complex samples, their use in solubility measurements, and activation methods for trace impurities. Aten (7) has reviewed the application of tracers in analytical chemistry and has given several examples. Activation and neutron absorption methods are also considered. Tordai (177) has reviewed the use of tracers in inorganic analysis. The methods of inorganic analysis, activity analysis, and activation analysis are given with examples. Tordai (176) has also discussed the use of tracers in the analysis of organic compounds chiefly as an aid to industry. Gordon (68) has reviewed the use of nucleonics in analytical chemistry for 1947 and 1948. Fleischmann (57) has given a general review of the applications of radioactive isotopes. Yankwich (192), in a discussion of the isotope dilution method, has shown that radioactive isotopes, especially of the light elements, differ somewhat from normal mixtures of stable isotopes in their properties.

For the use of radioisotopes in biochemical and biological work Dechambre (38) has described counters and sources of isotopes, as well as the choice of the appropriate isotope for various purposes. Hevesy (83) has given an historical sketch with an excellent bibliography of the biological application of tracer elements. Weygand (185) has also given a general review and has considered dilution analysis and the choice of suitable isotopes. An extensive bibliography is given covering the period from 1923 to 1948. Neuert (127) has also reviewed the use of radioactive tracers and has given several examples of the application of tracer methods in biology and metallurgy. Kirk & Duggan (99) have reviewed the literature for 1949 with emphasis on the use of tracers in biochemical analysis. The determination of naturally occurring radioactive elements was reviewed by Rodden (144). Swallow (164), Rosenblum (145) and Irvine (89) have reviewed the applications to industry but there is not too much analytical work described. Although radioactive measurements with nuclear emulsions do not lend themselves to great accuracy, at times they may be of use (134). Yagoda (190)

collected this literature in book form. Jech (91) detected radioactive atoms in the air while Broda (18) detected radioactive samarium, lead, bismuth, radium, thorium, and uranium, by embedding the samples in the emulsion. Coppens (29, 30, 31) has determined the uranium and thorium distribution in rocks. Drobkov (40) used the photographic plate method in his work on the need of radium, thorium, and uranium in plant life.

Chemical Determinations

Amino acids.—The property of amino acids to form complex compounds with copper was used by Wieland *et al.* (188) for a quantitative determination of α-amino acids. By using Cu^{64} (12.8-hr.) the analysis was carried out by measuring the activity of strips cut from paper chromatograms. In somewhat similar work Blackburn & Robson (11) tagged copper phosphate with Cu^{64} and then counted the resulting amino acid complex with an end-window Geiger-Müller counter.

Actinium.—Lecoin *et al.* (106) described procedures used in the Laboratoire Curie for measuring the quantity of actinium or actinium disintegration products by means of either beta or alpha radiation.

Antimony.—See *Tin.*

Astatine.—Garrison *et al.* (65) have isolated astatine from organic substances by coprecipitation with metallic tellurium or by deposition on silver foil. Both methods can be used for quantitative analysis but the silver foil method is simpler.

Barium.—See *Strontium.*

Bromine.—In a technique reported by Winteringham (189), good results were obtained by precipitating as silver bromide and coagulating by rotation. The precipitate is washed with acetone and pressed on a lead disc so that the filter paper can be peeled away. The metal disc simplifies the weighing and handling of the precipitate. In a method employing the same precipitation reagent, Daudel *et al.* (36) showed their average error of recovery to be 4.5 per cent. In order to decompose organic material Daudel *et al.* (37) have used a micro Parr bomb and after acidifying with nitric acid have precipitated the bromine with silver nitrate. The activity of the radioactive silver bromide is then measured with a Geiger-Müller counter.

Calcium.—In some interesting experiments on the determination of Ca^{45} by Shirley *et al.* (157) the effect of various impurities and precipitation forms on the counting rate was shown. Although calcium oxalate shows somewhat higher beta particle absorption than calcium carbonate, the oxalate was found more satisfactory as a precipitating agent since it effected separations from interfering elements such as aluminum and phosphate when present alone. When aluminum and phosphate ion were present together large discrepancies in weight and in specific activity were observed.

Carbon.—As would be expected there was considerable activity in the C^{14} field. As noted under reviews above, there have been several books and review articles devoted to C^{14} analysis.

Roberts *et al.* (142) have described an apparatus for the separation of C^{14} in which the carbon dioxide from a combustion train is converted to barium carbonate. The precipitated carbonate is washed and filtered on paper supported by a glass frit. The above operations are performed in a single enclosed apparatus. The filter paper is then dried and measured with a modified Lauritsen electroscope. For a rapid semimicro method Harper *et al.* (76) have described a barium carbonate precipitation method in which four samples per hour can be readily analyzed. For handling the barium carbonate precipitate Armstrong & Schubert (5) used a small shallow Büchner-type funnel made of brass which fits under a thin window counter.

In three papers Claycomb *et al.* (24, 88, 182) have described techniques for C^{14} analysis. An apparatus for the wet combustion of organic compounds with high efficiency is described; blank values are negligible and adequate control over gaseous carbon dioxide is maintained. With the range of combustion efficiency (90 to 95 per cent) obtained, it is possible to add carrier carbon either before or after combustion. The introduction of samples and the mixing of constituents is mechanically simple. A centrifugation technique for separation of barium carbonate gives smooth sample surfaces, uniform and free from cracks, with which consistent reproducible specific activities are obtained. When samples were protected from atmospheric carbon dioxide contamination a mean recovery of 97.7 per cent was obtained. Reproducibility of the plating procedure for identical samples gave a relative probable error of 0.60 per cent. With constant activity and varying amounts of carrier a relative probable error of 1.89 per cent was obtained. An apparatus for the synthesis of C^{14} labelled compounds is also described.

Beamer & Atchison (9) used infrared spectrophotometry to determine the chemical purity of the C^{14} compounds. Techniques and apparatus for handling small amounts of C^{14} labelled compounds of high specific activity are also described with a deviation in the counting of the barium carbonate of ± 10 per cent. White (186) described an apparatus for the analysis of C^{14} in barium carbonate samples obtained from tissue oxidation. The carbon dioxide, which is analyzed by a slight modification of Miller's method (119), is liberated by perchloric acid, the water removed at $-80°$, and the carbon dioxide condensed at $-195°$C. After measuring the volume of carbon dioxide a predetermined quantity of carbon disulfide vapor is added and this mixture is then counted. Eidinoff (47) has made a thorough study of the carbon dioxide-carbon disulfide method and has found that in the 1 to 4 cm. pressure range of carbon dioxide the average deviation for 11 measurements is 1.2 per cent. At a total pressure of 50 cm. the average deviation of seven measurements was 0.4 per cent. The gas trains and apparatus used showed negligible "memory" effects (contamination from previous runs).

An interesting application of C^{14} is in the determination of the age of archaeological samples by Arnold & Libby (6). The C^{14} formed by bombardment of the nitrogen in the air by cosmic rays is converted to $C^{14}O_2$ and then into wood or other growing organic substances. On death of the growing

substances the C^{14} decays without renewal. Samples (1 oz.) of trees excavated from the ground as well as articles of furniture of Egyptian origin, of known dynasties, were burnt and the carbon dioxide formed was reduced to elementary carbon by hot magnesium metal. The carbon formed was spread over the surface of a screen wall counter and measured. By comparison of the C^{14} present with that present in equilibrium amounts in living material the age of the object can be determined from the half life of C^{14} of 5,720 years. The agreement between predicted and observed ages was satisfactory.

For the direct determination of C^{14} in fatty acids, Entenman *et al.* (49) mounted the fat samples directly on paper-covered aluminum discs. They state that the error is no greater than 5 per cent. For the combustion of C^{14}, Reid & Tietz (140) used a small Parr bomb with sodium peroxide.

Cerium.—Freedman & Hume (61) have developed a rapid method for the estimation of small amounts of cerium in mixtures of rare earths based upon the separation of part of the cerium in pure form, followed by a spectrophotometric determination of the cerium and a measurement of the efficiency of the recovery process with a radioactive cerium tracer. The method is accurate to about 1.8 per cent. The technique employed is discussed as a general method for the determination of trace amounts of elements.

Hydrogen-tritium.—Aĭvazov & Neĭman (2) have made, unfortunately in Russian, a survey of the literature on tritium, giving analytical methods for its determination. Melander (118) has devised a method, not requiring high-vacuum pumps and liquid air, for tritium determinations which is accurate to ± 2 per cent. The tritium sample, if water, is reduced to the element over hot magnesium and the active gas is introduced with methane into a Geiger-Müller counter. He showed that the measured activity is proportional to the amount of tritium present in the counter tube. Eidinoff & Knoll (48) plated out an organic compound on a sample pan and then counted it in a windowless counter. The time-consuming combustion was eliminated and the compound was not destroyed. The principal disadvantage arises from the weak beta particles emitted by the tritium.

Cobalt.—See *Strontium.*

Iodine.—See *Strontium.* Raben (137) determined iodine by oxidizing to iodate with bromine or permanaganate. The iodate formed was allowed to react with labelled iodide. The iodine formed was extracted with carbon tetrachloride and the I^{131} measured by gamma ray counting in glass vials. The method can be used since the exchange of iodine atoms between iodide and iodine is rapid whereas between iodate and iodine or iodide does not occur. The method gave good results in the range of 0.1 to 2 μg. of iodate. Nesh & Peacock (126) used radioactive iodine to show the recovery of iodine in the analysis of protein-blood iodine. The colorimetric iodine determination in the distillate was corrected by using radioiodine to show recovery obtained. Lewis (107) used a continuous extractor with carbon tetrachloride and determined the radioiodine in a high pressure ionization chamber. The chemical yield was obtained by the Volhard volumetric method. For the

analysis of microgram quantities of amino acids, Keston *et al.* (98) treated a mixture with an isotopic reagent to form quantitatively a radioactive derivative of the desired amino acid. A large excess of the unlabelled derivative is added as a carrier and is then purified to constant isotope concentration. From the specific radioactivity of the purified carrier as well as the fraction of the carrier remaining after purification the quantity of amino acid present in the original mixture could be determined. For the analysis of urinary I^{131} after tracer and therapeutic doses Freedberg *et al.* (59) employed four Geiger-Müller counters around the circumference of a circle with the urine sample in the center. No doubt the high pressure gamma chamber (13) could be used in place of the four counters. Edwards *et al.* (45) employed a dipping counter for the determination of I^{131} in urine. For the detection of trace amounts of I^{131}, Fields & Pyle (54) add iodine as carrier and eventually extract the iodine with carbon tetrachloride. The purified iodine is precipitated as silver iodide and counted.

For the estimation of short-lived free radicals, Durham *et al.* (43) employed iodine labelled with I^{131} and formed alkyl iodides which are frozen out in liquid air. After separation by fractional distillation and conversion to silver iodide the sample is counted and the relative proportion of the radical initially present is determined.

Ionium, Protactinium, and Polonium.—Katzin *et al.* (95) analyzed ore residues for ionium, protactinium, and polonium with the aid of a suitable choice of carriers. Manganese dioxide formed *in situ* will carry polonium quantitatively. Ionium is carried by thorium when precipitated by hydrofluoric acid, and zirconium phosphate will carry protactinium as well as ionium.

Iron.—Haenny *et al.* (73) separated Fe^{59} from radioactive cobalt and phosphorus by hydrochloric acid-ether separation.

Polonium.—Prestwood (135) has described the procedure and apparatus for electroplating polonium on a platinum electrode in an atmosphere of hydrogen. A yield of 94 per cent was obtained.

Potassium.—Although the half life of K^{40} is quite long (15×10^8 years), potassium has been determined in solids with a Geiger-Müller counter by Gaudin & Pannell (64). By counting for a sufficiently long period of time, samples assaying as little as 0.1 per cent can be analyzed. The main effect of $\dot{K}^{40}$, however, is as a nuisance in prospecting for thorium and uranium by counting methods where potash-bearing rocks frequently give erroneous results. Senftle (154) has investigated this and also analyzed for potassium by this method. Tiratsoo (172) states the radioactivity of sedimentary rocks is largely related to the potassium content.

Protactinium—See *Ionium* above. Russell (150) has determined protactinium in urine by converting to the chloride and then extracting the chloride with diisopropyl ketone. Pa^{233} is used as a tracer and the protactinium content of the urine determined radiometrically.

Phosphorus.—The use of P^{32} as a tracer in plant material has resulted in

a considerable amount of work on this isotope. Hall & MacKenzie (78) have reviewed its use and have indicated that considerable adsorption occurs on glassware. They recommend coating apparatus with dimethyldichlorsilane or butylmethacrylate. The phosphorus is filtered as $MgNH_4PO_4 \cdot 6H_2O$ directly on a suitable holder. They point out the need of permanent standards. Rubin (147) has also pointed out the adsorption on glassware and recommended 2 per cent "Dow DC200" in pure carbon tetrachloride as a coating medium. McAuliffe (111) employed a solution-counting technique and stated that an accuracy of 1 per cent was obtained. Factors influencing the count such as K^{40} background, temperature, self-absorption, and adsorption on glassware are discussed. MacKenzie & Dean (113) avoid the adsorption effects by briquetting the material and then counting. Potassium does not create any difficulty unless the P^{32} activity is low. Borell & Holmgren (12) have used P^{32} for the assay of thyrotrophin. For the measurement of phosphate esters which have been separated on paper chromatograms Boursnell (14) has developed a "scanning" device.

Radium.—For the rapid assay of uranium ore process solutions Ames *et al.* (4) precipitated the radium with barium as a carrier. In chloride solutions the barium-radium chloride is precipitated with hydrochloric acid and ether, while in sulfate solutions $(Pb\text{-}Ra)SO_4$ is first precipitated followed by a $(Ba\text{-}Ra)SO_4$ precipitation. The sulfate is used as a counting form in a parallel plate ionization chamber. An accuracy of 3 to 10 per cent is claimed and the elapsed time is 30 to 60 min. A somewhat similar method is reported by Russell *et al.* (149) for radium in humans. The procedure is given in detail. Cation exchange resin may also be used to separate the radium. In another method using the radon emanation method (55), the radon produced in a measured time is transferred into an alpha ionization chamber. This is in much the same manner as usually employed (144). Jacobi (90) has also employed the radon emanation method for determining radon and radium in water.

Radon.—See *Radium.* Gübeli & Kolb (72) have described a circulation method for determining radon and thoron which is a modification of older methods (144). Drigo (39) has determined radon with the aid of a scintillation counter by measuring the activity of solid disintegration products of radon after collecting on a negatively charged electrode. Thorburn & Healy (171) determined radon in water by separating the radon daughters and counting with a beta counter.

Sodium.—Forbes & Perley (58) have determined the total body sodium in man by using Na^{24} as a tracer. The Na^{24} was injected intravenously and after 18 hr. for extravascular sodium to equilibrate, the serum was analyzed.

Strontium.—Duncan *et al.* (42) developed a method for the measurement of radioactive strontium, barium, cobalt, and iodine in river water. Each element is separated chemically and determined by beta counting. For strontium and barium combined, sodium carbonate is added and the water evaporated. After separating the carbonates they are counted. For strontium and

barium separately, the usual chromate method is employed. Cobalt is extracted as the ammonium cobaltothiocyanate with an amyl alcohol-ether mixture. Cobalt is then precipitated as ferrocyanide and counted. Iodine is extracted with carbon tetrachloride and precipitated as silver iodide for counting.

Sulfur.—Young *et al.* (193) have measured S^{35} in biological materials by oxidizing with the Carius method followed by precipitation of benzidine sulfate which is then measured in an ionization chamber. Mean recovery of S^{35} was 99 per cent and the standard deviation of a single measurement was 2.8 per cent.

In an indication of the industrial use of S^{35}, Eaton *et al.* (44) prepared radioactive pyrite from S^{35} and were then able to trace the sulfur in a full scale coking operation. Techniques for counting are described.

Thorium.—See *Uranium.* Koczy (100) employed the emanation method for determining thorium by measuring the thoron removed from a solution by bubbling. Gübeli & Kolb (71) have investigated the effect of inactive salts on the activity from solid thorium oxalate, thorium oxide, and thorium nitrate. Moeller & Schweitzer (122) determined thorium by precipitating with an excess of pyrophosphate of known P^{32} activity and, after filtering, measured the excess activity left in the solution. The solubilities of the pyrophosphates of several rare earths and thorium were measured.

Tin.—Cook (27) has described methods for the analysis of tin and antimony in fission products. The electrolytic formation of stibine is recommended for antimony.

Uranium.—See *Radon, Radium,* and *Thorium.* Although there are several articles on the use of counting for the determination of uranium in rocks, for a reliable determination the chemical method is still preferred. Szalay & Csongor (165) measured the radioactivity of rocks with a commercial Geiger-Müller counter shielded by lead with correction made for cosmic radiation. The uranium content was estimated from the dimensions of the counter.

Kuroda (104) states that uranium and thorium in radioactive minerals are easily distinguished by measuring the emanation given off with an I. M. Fontactoscope. Thommeret (170) estimated the uranium content of minerals, which were free of thorium, by measuring the beta and gamma radiation with separate samples. Because the ratio of radium to uranium varies in different minerals, a single measurement gives little information. However, gamma rays come almost entirely from radium and its descendants, while beta rays come from UX_1 and radium descendants. Hence the simultaneous measurement of beta and gamma activity. The apparatus is calibrated by empirical means. It is stated that uranium content higher than 0.1 per cent could be determined with an error of ± 10 per cent. Senftle & McMahon (156) have determined uranium in the field with suitable standards and standardized trays and counters.

Horwood & McMahon (85, 86) have used a high pressure ionization chamber (13) in assaying ore samples for uranium. The apparatus has been

used for 12 months with consistent results. In some preliminary experiments Haney (79) has used gamma counting for the continuous radioactive assay of ores and mill products. The range was from 0.006 to 0.5 per cent uranium oxide. Marble (117) has reviewed the literature for 1948 and 1949 in his report on the measurement of geologic time. Festa & Santangelo (53) described problems connected with geological radioactivity determinations. Nogami & Hurley (128) have measured combined uranium and thorium by alpha ray counting of thick layers of the sample in an ionization chamber of large sample area. Corrections are made for absorption factors. Rothstein *et al.* (146) have determined the uranium content of biological materials. The samples after ashing are dissolved and precipitated using calcium phosphate as the carrier. This is then followed by an ether extraction of the nitrate. The uranium is finally electroplated on silver and the alpha activity measured in a parallel plate pulse chamber.

Zirconium.—In a review by Hume (87) on radiochemical activity analysis, methods for the analysis of zirconium activity are discussed in detail. Methods for the separation from fission products are given whereby zirconium is precipitated with barium as the carrier. The barium is removed by precipitating as a sulfate and the zirconium precipitated with cupferron and after ignition to oxide the activity is measured.

Activation and Absorption

Boyd (15) reviewed the methods of activation analysis as applied to analytical chemistry and came to the conclusion that the widespread use of activation analysis appears to hinge upon the emergence of apparatus of relatively modest cost for laboratory production of artificial radioactivity. As a result of this, the work has been limited to those institutions having a high flux of activating particles. His review gives an excellent idea of the possibilities and present limitations. A discussion of activation sources, feasibility of the method, and examples of analyses performed are presented. He has epitomized the method as follows:

> Irradiate a sample of the substance to be analyzed together with a standard sample containing a predetermined weight of the element to be determined. Dissolve the samples and add to the solutions a known weight of the element whose radioactivity is to be measured. Chemically process the added element so as to free it from the bulk constituents in the sample and to remove quantitatively any contamination radioactivities produced in other elements present in the unknown. Determine the chemical yield of the procedure. Compare the activity from the unknown with that from the standard. As a check on the radiochemical purity of the assay samples it may be desirable to measure their half lives and to characterize their radiations by means of aluminum or lead absorption curves, or otherwise.

Taylor & Havens (81, 168, 169), in an important series of articles, have reviewed the use of neutron spectroscopy in chemical analysis. A general review of the properties of neutrons, the nature of their reactions, and the methods by which their interaction as a function of their velocity or wave

length could be measured was followed by descriptions and illustrations of the application of resonance absorption and scattering of neutrons. Examples were given as applied to analytical chemistry. In these instances, however, the equipment is still more elaborate and complicated than given by Boyd for activation analysis and is therefore limited to the few locations which have access to this equipment. Its application on a large scale is definitely out of the question at the present time. In the third article (169) by Taylor & Havens, absorption by a beam of thermal neutrons is used to analyze materials. A rather complete review of this method is given and examples of the determination of boron in boron carbide, water, and hydrogen in metals, etc., are given. The use of activation methods is also discussed.

Smales (159) has reviewed radioactivation methods giving techniques and neutron sources. Of interest in this type of analysis is the bibliography on radioactive neutron sources by Croxton (32) and activation produced by thermal neutrons by Senftle & Leavitt (155). Muehlhause & Thomas (124) have discussed the use of the pile for chemical analysis. Analysis by neutron absorption as well as activation can be made. As an example, 10 p.p.m. of hafnium in zirconium was determined with a 1-min. bombardment. Smales & Brown (160) have determined fractions of a part per million of arsenic in germanium by radioactivation analysis. The germanium oxide was irradiated for 24 hr. converting arsenic to As^{76}. After dissolving in sodium hydroxide the arsenic was distilled as arsenic trichloride, precipitated as metal, and then counted. A 0.2 p.p.m. limit was indicated. Kohn & Tompkins (102) applied neutron activation methods to the analysis of rare earths. A small sample was irradiated in the Clinton reactor and was then counted. By this procedure 0.63 per cent of samarium in cerium, 1.18 per cent of dysprosium in yttrium, 0.023 per cent of neodymium and, 0.01 per cent of cerium in praseodymium, and 0.03 to 0.3 per cent of cerium in lanthanum have been determined. To give an indication of the thoughts in this method of analysis, a patent has been given to Lipson (110) for determining hydrogen by slowing down of fast neutrons in the material. Brown & Goldberg (19, 20) determined gold and rhenium in iron meteorites by the pile irradiation method. After exposure to thermal neutrons, Au^{198}, Re^{186}, and Re^{188} are formed. The sample is dissolved, the gold reduced with quinol, and the rhenium is then precipitated as Re_2S_7. Auric chloride and potassium perrhenate were used as carriers. The gold is finally mounted as metal and the rhenium as tetraphenylarsonium perrhenate. Comparison is made with standards. The gold values ranged on different meteorites from 0.7 to 3.6 p.p.m. and the rhenium from 0.3 to 1.6 p.p.m.

Süe (162) used neutrons from a radium-beryllium source screened with cadmium to determine boron, cadmium, silver, and lithium in silica and cadmium in zinc by absorption of thermal neutrons. An interesting use of activation methods is that of Pannell & Freyberger (132) who used the γ, n reaction for analyzing and picking beryl. As little as 0.01 per cent beryllium oxide could be analyzed by a 1 gm. radium source.

Facchini & Orsoni (50) irradiated minerals with thermal neutrons and determined the uranium content by the fission of the U^{235} present.

Theoretical Analytical Chemistry

As Kolthoff remarked at the summer symposium on Analytical Chemistry in June of 1950, not enough attention is being paid to the theory of analytical chemistry. The following groups are more or less in the theoretical category but are definitely of interest to the analyst because they give information on certain phases which have a tendency to be neglected. In the precipitation of lanthanum as fluoride, zirconium has a tendency to be carried along. Gest *et al.* (66) used Zr^{95} as a radioactive indicator and showed that surface adsorption was primarily responsible for the coseparation of zirconium. The adsorption was found to be reversible, to be independent of the fluoride ion concentration from 0.1 to 1.0 *M* and of the nitric acid concentration from 0.3 to 1 *M*, and was also unaffected by temperature. In studies on the tracer chemistry of actinium, McLane & Peterson (112) showed that the carrying of actinium by zirconium iodate is sensitive to the iodate concentration varying from less than 10 per cent to over 90 per cent. Neutral salts decrease the carrying. Lanthanum fluoride and hydroxide carried actinium quantitatively while lanthanum oxalate precipitated from strong acid was depleted in actinium.

In order to determine the efficiency of separation of pyrophosphate from orthophosphate as zinc pyrophosphate, van der Straaten & Aten (183) used a radiochemical technique, employing radiophosphorus. It was found that the method of separation was satisfactory. Haenny & Mivelaz (74) studied the electrolytic separation of zinc by using Zn^{65}. The separation was demonstrated to be dependent on the electrode used, a certain amount being left in solution. In an interesting angle on an old subject, Turner (179) used radioactive iodine to show that starch blue does not contain iodine. She concluded that the change leading to the blue color is a change induced in the starch molecule by iodine acting catalytically in the presence of oxygen.

Ruka & Willard (148) used radiobromine for the determination of the solubility of silver bromide in nitric acid. Langer (105) used radioactive silver as an end-point indicator in argentometric titration. In order to cut down the time necessary, a method is employed whereby only two points on a branch of the titration curve are measured. Exchange studies with silver halides were made. The method could be used in determining the total amount of silver in an unknown mixture of silver chloride, bromide, and iodide without the necessity of isolating a particular halide or electrolyzing the total silver.

Joris & Taylor (92) used tritium in the determination of the solubility of water in solvents. An example given was the solubility of water in benzene. Brickam *et al.* (17) used an ion exchange method for the separation of tracer quantities of rhenium and osmium from large amounts of tungsten using Amberlite IR-4, while Yang (191) used radioactive tracers for ion resin ex-

change separation of lanthanum and yttrium. Haissinsky (77) has discussed the electrochemistry of natural and artificial radioelements and has reviewed the theoretical aspects.

Hahn (75) has reviewed his emanation method and has drawn attention to the many uses to which it may be put. The emanation of natural radioelements, radon and thoron, have been used to investigate the molecular state of compounds, their inner surfaces, or their deformations resulting from aging, as well as molecular and chemical conversions. The thermal behavior of certain salts are given which are tied in with x-ray findings. It would appear that the method has certain possibilities which have been neglected by the chemist and the article is well worth studying.

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ATOMIC AND MOLECULAR SPECTROSCOPY[1]

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Scope

Only those spectroscopic results will be dealt with here which have some relation to the mass or structure of the nucleus or which were made possible by activities in the atomic energy field such as the separation of isotopes or the production of artificial elements. Occasionally it seems appropriate, in order to present a well-rounded picture, to include some results which might have been omitted under a strict interpretation of these criteria. The literature references at the end of the chapter contain many papers with pertinent results which could not be mentioned in the text because of lack of space.

Spectroscopy is understood here to mean the techniques dealing with the wavelengths from the ultraviolet through the visible and infrared to the microwave region. Although the magnetic resonance methods are quite different in their experimental aspects from the typical spectroscopic methods such as employed in the visible, the type of results obtained with such methods is so similar to the results of the regular spectroscopic methods that it seems best to include them here. Thus no limitation is placed at the low-frequency end. On the other hand, x-ray spectroscopy which gives information about the inner electron shells or γ-ray spectroscopy which penetrates into the interior of the nucleus are excluded.

The various sections have not been treated with equal thoroughness. More details have been given in the first three sections whereas the latter ones are not much more than a guide to the bibliography. This expresses no opinion as to the importance of the various parts. It was felt that a more or less well-rounded presentation of some parts as, for instance, one-electron spectra, can be given now, whereas other parts as, for instance, microwave and radio-frequency spectra, are still in such a rapid stage of development that an attempt to summarize them should be left for a subsequent volume. To do the whole subject justice in the limited space available was obviously impossible.

One-Electron Spectra

Bohr, by giving an interpretation of the spectrum of the hydrogen atom in 1913, started the modern theory of atomic structure and of the interpretation of spectra. While Bohr's theory gave for the first time a convincing quantitative account of the structure of any spectrum, details were subsequently discovered in the structure of the hydrogen lines which gave rise to a long sequence of investigations and led to very important extensions of the theory of atomic structure. This development came to a successful conclusion

[1] This review is essentially a survey of papers published in 1950.

during the past few years and for the first time it is possible to give a theory of the hydrogen spectrum which seems to be in substantial quantitative agreement with all the known facts.

Because of the fundamental importance of these developments it may be useful to give here a recapitulation of our knowledge of the atomic hydrogen

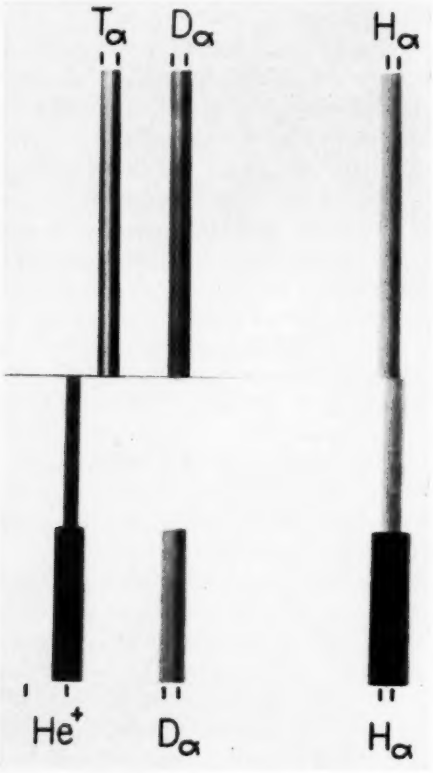

FIG. 1. Upper Part: The 3→2 transition showing isotopic displacement for atomic tritium, deuterium, and hydrogen. Fine structure partly resolved. It is evident that the T_α line is much sharper than H_α because of decreased Doppler broadening.

Lower part: The 6→4 transition of He^+ with D_α and H_α as reference lines (Photo: Byrne, Johns Hopkins University).

spectrum. An atom with only one electron is the only one for which the energy levels can be calculated without undue mathematical complications. For this reason, discrepancies between theory and experimental facts, no matter how small, must be significant and indicative of some fundamental shortcoming of the theory or possibly of the experimental technique. In the more complex spectra such discrepancies can often be attributed to inadequacies in the mathematical method of approximation.

Figure 1 is the reproduction of H_α and its analogous lines in deuterium, tritium, and ionized helium, taken with a large grating. After Balmer in 1885 had found the first spectroscopic regularities it was not until 1913 that an adequate theoretical explanation was found by Bohr.

The formula

$$\nu = RZ^2\left(\frac{1}{p^2} - \frac{1}{q^2}\right)$$

with

$$R = \frac{2\pi^2 me^4}{h^3 c}\left(1 + \frac{m}{M}\right)^{-1}$$

for a $p \rightarrow q$ transition which emerged from Bohr's theory for any line of a one-electron spectrum gave also the mass shift between different isotopes. This was first confirmed by a comparison of the H and He^+ spectra and contributed greatly to the acceptance of Bohr's theory. Figure 1 illustrates this also for the heavy hydrogen isotopes which were discovered later.

While such experiments firmly established the Bohr theory as the guiding principle for the interpretation of spectra, other experimental facts about the hydrogen lines were found which did not have such an easy explanation.

Figure 1 shows that H_α appears as a doublet, a fact first discovered indirectly in 1887 by Michelson. The structure of D_α and T_α is identical except for the greater sharpness of the lines in the heavier isotopes (resulting from reduced Doppler broadening). The corresponding He^+ lines, however, have a wider and more complicated structure which was revealed by Paschen in 1918, in particular for the $4 \rightarrow 3$ line.

It is well known that Sommerfeld interpreted this fine structure by taking into account that in a Coulomb force field the electronic orbits can be ellipses. Ellipses with the same major axis have the same energy independent of the excentricity of the orbit. If the speed of the electron, however, is such that it cannot be neglected compared to the velocity of light, ellipses with different excentricities have slightly different energies. Sommerfeld showed that a relativistic treatment of the motion would account quantitatively for the observed fine structures in hydrogen and ionized helium.

These very important results stimulated a great deal of experimental work intended to get a better picture of the empirical fine structure of the hydrogen lines, particularly that of H_α. This interest was intensified when, with the discovery of the spin of the electron, it was revealed that Sommerfeld's theory had given the correct results only because of two errors, unavoidable at the time, which nearly cancelled each other. (These were: neglect of the electron spin and neglect of refinements of quantum mechanics.) The theory of the electron by Dirac (1928) which was consistent with all the developments gave essentially the same results as the Sommerfeld theory, but where there were discrepancies between the results of the two theories, the Dirac theory agreed better with the experimental facts.

The experimental study of the hydrogen fine structure had shown that

extreme care is necessary to obtain reliable results. Figure 1 shows the appearance of the lines with a large grating but without attempts to control the discharge to obtain lines of maximum sharpness. The theory had shown that H_α should consist actually of five components as indicated in the lower part of Figure 2. Because of the great differences in intensity and the close spacing of the components complete resolution is not possible. What is observed in Figure 1 is the superposition of 1+4+5 and of 2+3. It should, however, be

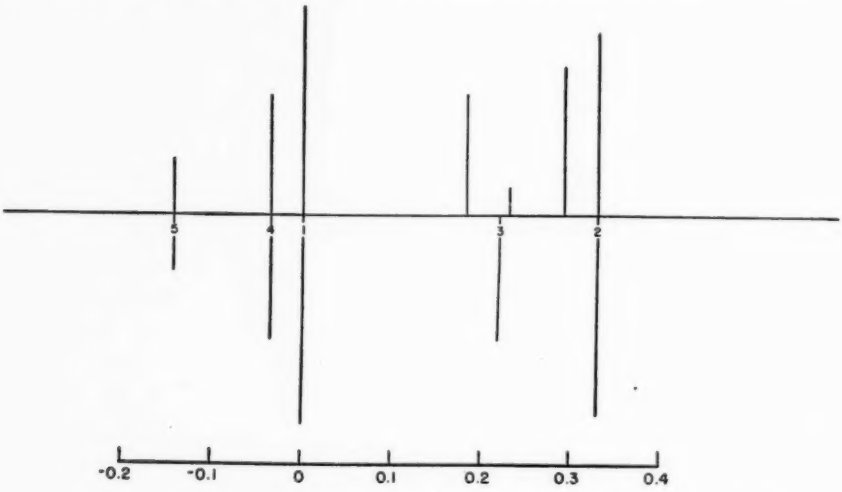

FIG. 2. Structure of H_α according to Dirac's theory (lower part), and with the S shift taken into consideration (upper part).

possible to separate 2 from 3 as this requires a resolving power of about 150,000, which is within the possibilities of a large grating. In order to be more independent of instrumental limitations, most of the fine-structure investigations were made with an interferometer. The chief limitations are then the finite width of the line chiefly resulting from Doppler and Stark effect broadening. Also self-reversal may be troublesome. The older inconsistent results were chiefly a result of such causes. Careful control of the light source was the chief concern.

The results obtained under the best conditions showed clear indications of the separation of components (2) and (3) but the separation (3)-(1) and (2)-(1) appeared to be smaller than the theoretical value. Pasternack (14) drew from this the conclusion that the $2S$ level must be shifted upward by a small amount. It seemed difficult to judge whether this small discrepancy was a result of imperfections in the experiments or of a real difference between theory and experiment.

New interest was concentrated on this problem when Lamb & Retherford in 1947 applied to it the molecular beam radio-frequency technique. Their

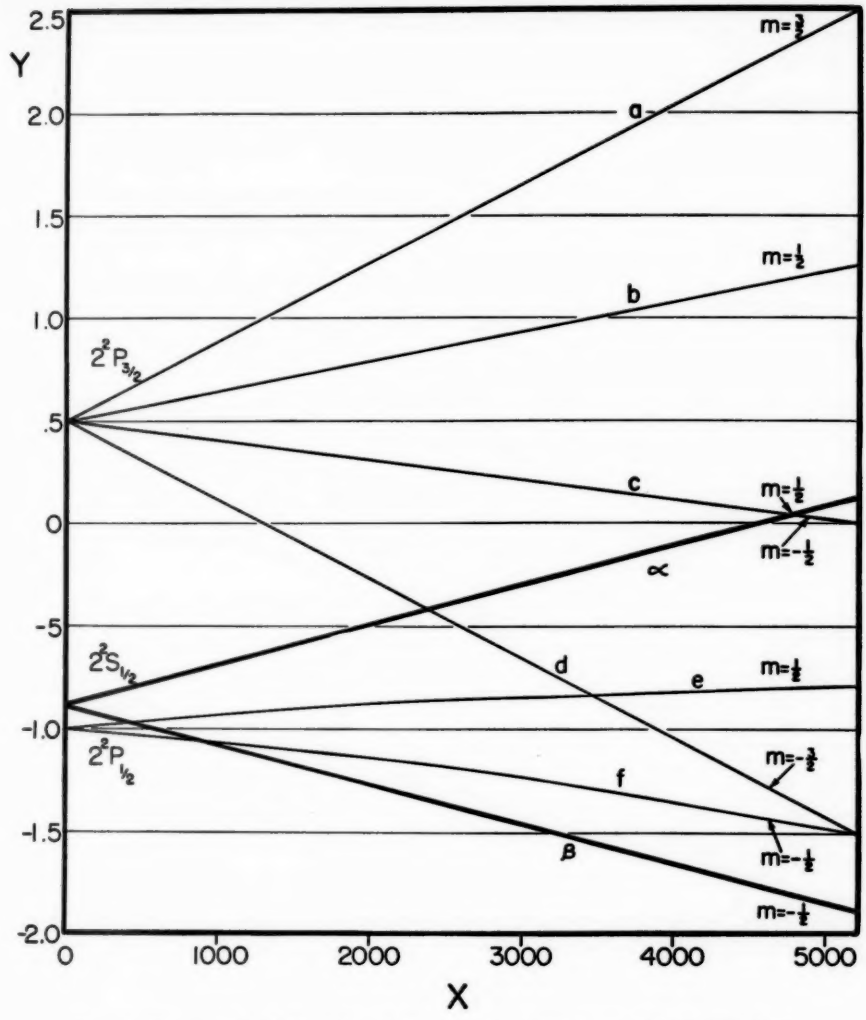

FIG. 3. Energy level diagram of the two-quantum state of hydrogen in a magnetic field (X in Oersteds) [after Lamb & Retherford (10)].

results proved beyond any doubt that the discrepancies indicated by the spectroscopic fine-structure measurements were real. They led to an important refinement in the fundamental theory. Lamb & Retherford's results are now being published in a series of detailed articles, the first two of which have appeared (10, 11).

The experiments were carried out as follows. The hydrogen atom has a metastable state $2S$ from which no dipole transitions can take place. If it is

possible to produce a large enough concentration of metastable $2S$ atoms, they will absorb those frequencies which will correspond to transitions to the $2P$ state. Such frequencies lie in the microwave region. (The $2S$-$2P_{3/2}$ frequency is 0.365_2 cm.$^{-1}$ or 10,948 megacycles; the $2S$-$2P_{1/2}$ frequency, which should be zero according to the Dirac theory, could be estimated from the discrepancies in the H_α fine structure to be near 1,000 megacycles.)

Lamb & Retherford carried out their experiment by producing hydrogen atoms in a tungsten furnace at 2,550°K. where about 64 per cent of the H_2 molecules are dissociated and then allowing the atoms to escape as an atomic beam into vacuum through a hole in the furnace. This beam is then subject

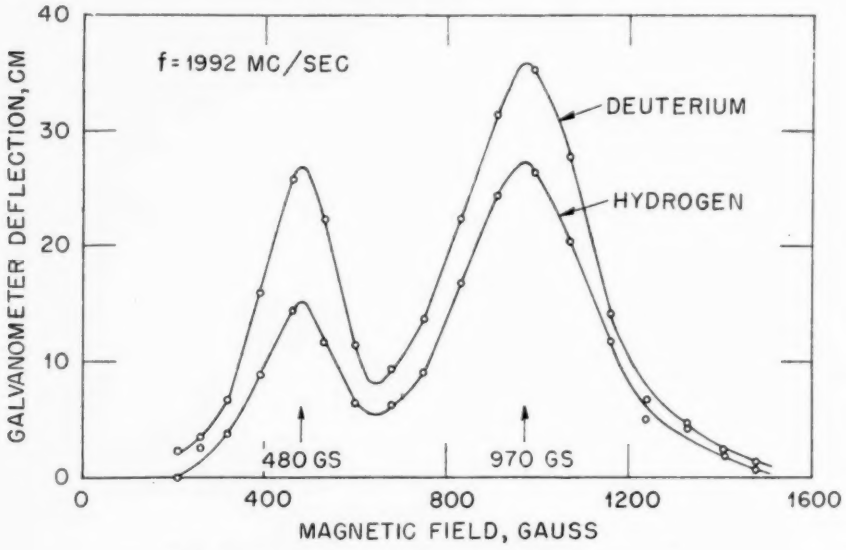

FIG. 4. Observed resonance curves in hydrogen and deuterium. From Lamb & Retherford (10).

to bombardment by electrons which produce many metastable $2S$ atoms. When these metastable atoms impinge on a metal surface, they eject electrons and this electron current can be measured. Hydrogen atoms in the normal state do not produce electrons. Other excited states which are also produced by the electron bombardment have such a short life ($\sim 10^{-9}$ sec.) that they disappear before they reach the metal surface.

If the beam is now subject to microwaves of the proper frequency, transitions to the $2P$ state take place which remove metastable atoms from the beam. This is measured as a reduction in the secondary electron current. This reduction plotted against the microwave frequency gives a typical resonance curve, the width of which is determined by the natural width of the $2P$ states and disturbing influences. (The actually found half widths were of the order of magnitude of 100 megacycles, a very considerable fraction of

the resonance frequency.) The registration of the resonance curve would normally be done by varying the microwave frequency except for the fact that with the present microwave techniques it is practically impossible to achieve this experimentally.

For this reason the atoms were placed in a magnetic field which splits the levels according to Figure 3. The $2S$ levels (α and β) have been drawn as heavy lines. It is now quite apparent that the distance between the $2S$ levels and the $2P$ levels to which they can make transitions because of microwave absorption is a function of the magnetic field. Any distance, i.e., any resonance frequency, can be obtained by choosing a suitable field strength. The experiment is, therefore, carried out at a fixed microwave frequency by plotting the resonance curve as function of the magnetic field strength.

The results are shown in Figure 4. The first peak at 480 gauss is the result of a transition from $2S(m=1/2)$ to $2P_{1/2}(m=-1/2)$, $(\alpha \rightarrow f)$, the second one to $2P_{1/2}(m=+1/2)(\alpha \rightarrow e)$. Taking similar curves for different frequencies gives assurance of the correctness of the interpretation.

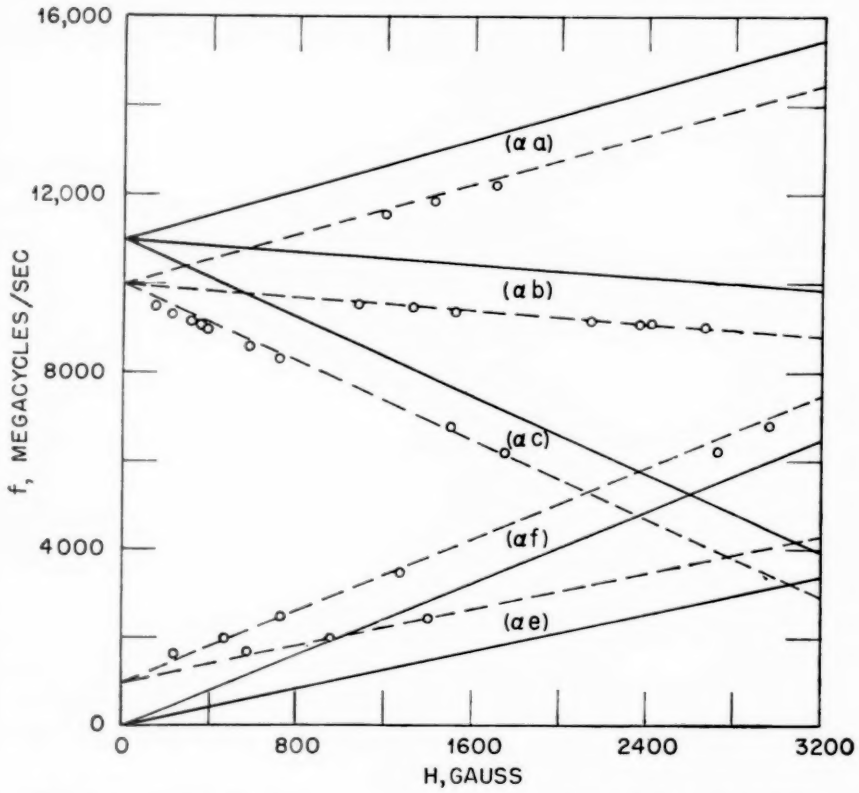

FIG. 5. Summary of results on resonance peaks [from Lamb & Retherford (10)].

FIG. 6. Interferometer pattern of D_α [from Kuhn & Series (9)].

Figure 5 gives a summary of Lamb & Retherford's results. The observed resonance frequencies are plotted as function of the magnetic field strength. The transitions are those from the $2S(m=+1/2)$ state to five of the six possible $2P$ states (labelled a–f as in Fig. 3). The points would have to fall on the solid lines if $2S_{1/2}$ and $2P_{1/2}$ would coincide as required by the Dirac theory. The dotted lines are those calculated under the assumption that the $2S_{1/2}$ state is 1,000 megacycles higher than the $2P_{1/2}$ state. It is seen that this is in good agreement with the observational points.

Later measurements (11) gave this $2S_{1/2}$-$2P_{1/2}$ shift as $1{,}062 \pm 5$ megacycles $= 0.03542 \pm 0.00017$ cm.$^{-1}$. By applying various corrections Lamb & Retherford expect to obtain a value of the shift accurate to one megacycle.

Recently the optical investigation of the fine structure of H_α was repeated by Kuhn & Series (9) under greatly improved conditions. In the first place they used D_α rather than H_α because of the smaller Doppler effect. They went to extremes in cooling the gas by using a discharge tube, the walls of which were mostly thin copper tubing, and this was directly immersed into liquid hydrogen (14° to 20°K.). The gas filling was 0.2 mm. deuterium and 1.7 mm. helium, the latter to give the hydrogen atoms a chance to lose kinetic energy by collision. The current was kept low (2 to 5 m.amp.) in order to avoid Stark effects and heating.

Under these conditions the lines were quite sharp. As Figure 6 shows, the weak component (3) (see Fig. 2) is clearly separated from the strong components (1) and (2), and, besides, there is also an indication of components (5) (not visible in Figure 6). The spacings measured are

(3)—(1)	0.1879 ± 0.0003 cm.$^{-1}$
(2)—(1)	0.3213 ± 0.0002 cm.$^{-1}$
(1)—(5)	0.138 ± 0.006 cm.$^{-1}$,

and from this the $2S_{1/2}$-$2P_{1/2}$ shift is found to be 0.0369 ± 0.0016 cm.$^{-1}$, which is in satisfactory agreement with Lamb & Retherford's value 0.0354 ± 0.0002. The accuracy of the magnetic resonance value is about 10 times better than that of the interferometric value.

We can summarize now that the recent investigations have shown that the observed H_α fine structure is in good agreement with the theoretical predictions, provided the $2S$ shift is included. The results of Lamb & Retherford which give this shift most accurately are in agreement with the optical results.

A quantitative theoretical explanation of the S shift was given first by Bethe (1) and the subject has since been treated repeatedly in theoretical papers (4, 6, 15). The Dirac theory of the electron neglected the interaction between the electron and the radiation field, whereas if such interaction is taken into account the S levels are shifted upward. The net value of the theoretically predicted $2S$ shift is $1{,}051.41 \pm 0.15$ megacycles (2). The discrepancy between this and the experimental value $1{,}062 \pm 5$ of Lamb & Retherford, though small, seems to be definitely outside the limits of experi-

mental errors. It is not certain now whether small systematic errors in the experimental procedure are responsible for the lack of complete agreement or whether small corrections have been neglected in the theoretical treatment. It is to be expected that this point will be cleared up soon.

It should be emphasized that the establishment of the S shift by Lamb & Retherford by no means has invalidated Dirac's theory of the electron. It has merely called attention to interactions formerly neglected which are necessary to implement the theory. The broadening of Dirac's theory has led to modern quantum electrodynamics.

The study of the atomic lines of hydrogen has thus furnished a powerful stimulus for the major developments in our fundamental theory of atomic structure. First it led to Bohr's theory of atomic structure. A little later it paved the way for the relativistic treatment. Later on it furnished one of the cornerstones of Dirac's theory, and finally the S shift provided definite material for the test of quantum electrodynamics.

The study of the fine structure of the He^+ lines has always gone together with that of the hydrogen lines (5, 7, 13). Conditions are similar except that the scale of the fine structure is 16 times that of hydrogen, and, therefore,

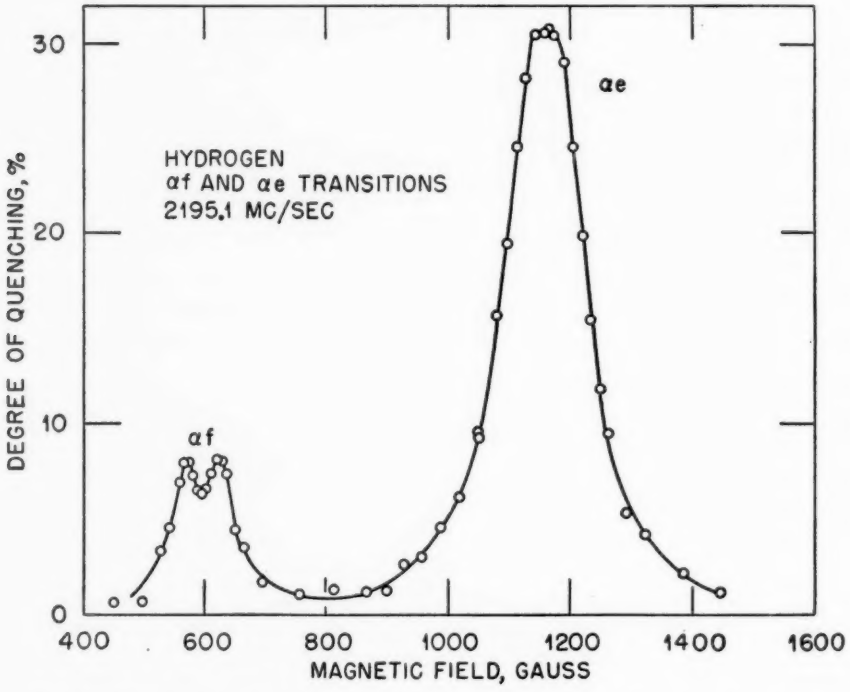

FIG. 7. Resonance peaks for hydrogen. The splitting of the αf peak is due to the magnetic moment of the proton [from Lamb & Retherford (11)].

resolution much easier. This, however, is compensated by the fact that excitation conditions are more difficult for He^+, but Lamb & Skinner (12) were able to obtain a shift by experiments similar in principle to those for hydrogen. Furthermore, those lines with the largest structure and the largest S shift lie in the ultraviolet where the accuracy is considerably less than in the visible. The results obtained with He^+ have, however, fully confirmed the hydrogen results.

For completeness' sake attention should be drawn here to the determination of the hyperfine structure in the atomic spectrum of hydrogen, the determination of the spin of the nuclei of the three hydrogen isotopes, and the measurement of the magnetic moments and the quadrupole moments of these nuclei. The hyperfine structure (262, 279) is much too small to be observed in the visible atomic lines. It shows, however, quite distinctly in Figure 7, obtained by the molecular beam resonance method. Very accurate measurements of the magnetic moments have been made by the various radio-frequency methods and some of these measurements could be used for improving the values of the fundamental constants.

In this connection should be mentioned also the precise determination of the gyromagnetic moment of the electron (265, 270) and its deviation from the theoretical value according to the simple Dirac theory.

All these spectroscopic measurements on very simple particles have been a strong stimulus for the development of modern atomic theory.

Production and Structure of Atomic Spectra

Since the first regularity was discovered by Balmer in 1885 in an atomic spectrum, great efforts were made to understand the arrangement of lines in the spectra of the elements. The discovery of the Rydberg-Ritz combination principle transferred the regularities in the arrangement of the lines to the terms which later were identified through the Bohr frequency relation with the atomic energy levels. In 1913 when Bohr's theory established the bridge between spectroscopy and atomic constitution, the structure of only the simplest spectra, chiefly those of the first three columns of the periodic system, had been recognized. Since then the theory of atomic structure and spectroscopy have mutually stimulated each other. This led to a very detailed picture of the structure of the electronic shell of all atoms, which was derived from the structure of their spectra. The guidance which atomic spectroscopy received from the ever-increasing knowledge of atomic structure made it possible to tackle with good assurance of ultimate success even the most complicated spectra.

The fundamental developments were essentially finished in the late twenties. This, however, does not mean that all spectra were analyzed at that time. Even now there are spectra the structure of which is completely unknown and many others for which only the crudest beginnings in the analysis have been made.

Table I, prepared by Meggers (57a), gives a concise summary of the

TABLE I*

State of Progress in the Analysis of Atomic Spectra

Spectrum / Element	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV	XV	XVI	XVII	XVIII	XIX	XX	XXI	XXII	XXIII	XXIV
1 H	bA																							
2 He	aA	bA																						
3 Li	bA	bB	eD																					
4 Be	bA	aA	cC	eD																				
5 B	cB	bB	bB	dC	eE																			
6 C	bA	bA	bA	bA	eD	-E																		
7 N	bA	bA	bA	cB	dB	-D	-E																	
8 O	bA	bA	bA	bA	cA	cB	-C	-E																
9 F	cA	cB	cB	eA	-B	-A	-C	-E																
10 Ne	bA	bA	eC	cB	-B	-C																		
11 Na	bA	cB	eB	-C	-C	-B	-A	-A	-B															
12 Mg	bA	aA	cB	eB	eB	-B	-B	-A	-A	-C	-E													
13 Al	aA	aA	aA	eB	eB	eB	-B	-B	-B	-C	-D	-E												
14 Si	bA	bB	bB	bB	eC	-B	-A	-B	-B	-C	-C	-D												
15 P	cB	cB	cA	cA	bA	-C	-B	-B	-A	-B	-C	-C	-D											
16 S	bA	bB	bB	cC	cC	cB	-C	-B	-C	-D		-E												
17 Cl	bA	cA	cB	cB	dC	dC	eC	-C	-C	-C	-E													
18 A	bA	bB	dC	eC	-C	-C	-D	-B	-E	-E	-E			-E										
19 K	bA	cC	cC	eC	-C	-C	-C	-C	-C	-C	-E													
20 Ca	aA	aA	cC	eC	eC	-C	-C	-C	-C	-C	-C	-D	-E		-E									
21 Sc	aA	aA	cC	-E	-D	-C	-D	-C	-C	-D	-C	-D												
22 Ti	aA	aA	cC	cC	-D	-D	-C	-D	-D	-E	-D	-B	-D											
23 V	aA	aA	cC	cC	dD	-D	-D	-D	-D		-E	-C	-B	-D										
24 Cr	bA	cA	dB	cC	cC	eE	-D	-D	-D			-E	-C	-B	-D									
25 Mn	bA	dA	dB	eC	dC	-D	eC	-E	-D	-D			-E	-C	-C	-D								
26 Fe	bA	cA	-A	-E	eC	-C	-C	-C	-E	-D	-D		-E	-E	-D	-B	-D							
27 Co	bA	cB	-B	-E	-E	-C	-C	-D			-D			-E	-E	-D	-C	-D						
28 Ni	aA	bA	-B		-E	-E	-C	-C	-D			-E	-E		-E	-E		-D						
29 Cu	bA	cA	-A				-E												-E					
30 Zn	aA	bB	dD	-E																				

Spectrum / Element	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV	XV	XVI	XVII	XVIII	XIX	XX	XXI	XXII	XXIII	XXIV
31 Ga	bB	bB	dD	dD																				
32 Ge	cB	cA	cC	cC	dD																			
33 As	cA	–C	cC	cC	dD	–D																		
34 Se	dB	–B	dC	–C	dD	dD	–B																	
35 Br	aA	eC	dD	dD	dD	–D	–E	–B	–D															
36 Kr	aA	cA	dB	–D					–D															
37 Rb	bA	cC	–C						–E	–B	–D	–E	–E	–E										
38 Sr	aA	bA		–D							–B	–D	–E	–E										
39 Y	aA	aA	dD		–B							–C	–D	–E	–E									
40 Zr	aA	aA	aB	cB		–B								–D										
41 Cb	dA	dA	dD	dB	–C	–D	–B																	
42 Mo	cB	dB	–D	–D	–C	–C	–D	–B								–E								
43 Tc	–B	–D																						
44 Ru	cB	cC																						
45 Rh	cB	cB	–C																					
46 Pd	aA	aA																–E		–E				
47 Ag	bA	bA	–B																–E		–E			
48 Cd	bA	bA	cA	–B																–E		–E		
49 In	bA	bA	cC	dD	–C																–E		–E	
50 Sn	cA	bA	cC	cC	dD	–C																–E		–E
51 Sb	dA	–C	cC	cC	dD	–E																	–E	
52 Te	dC	–D	–C	–D	dD	eD	–D																	
53 I	–C	–C	–E	–D				–E																
54 Xe	bA	–A	eA	–D																				
55 Cs	bA	dB	–D																					
56 Ba	aA	bA		–D																				

* Compiled by Meggers (57a).

† The present state (1950) is indicated by letters A to E where A means a fairly complete analysis and E that only a few lines have been classified, with B, C, and D intermediate between the two extremes. The small letters preceding the capitals present the state of affairs in 1932.

TABLE I*—(*continued*)

Element \ Spectrum	I	II	III	IV	V	VI	VII	VIII	IX
57 La	cA	bA	dA						
58 Ce	-E	-B	-B	eB					
59 Pr		-C							
60 Nd	-C	-C							
61 Pm									
62 Sm	-B	-B							
63 Eu	-A	-B	-D						
64 Gd	-B	-B							
65 Tb	-E	-E							
66 Dy		-D							
67 Ho									
68 Er									
69 Tm	-D	-C							
70 Yb	-C	-B	-D						
71 Lu	-C	-B	-D						
72 Hf	eB	dA							
73 Ta	-B	-B							
74 W	eB	-C							
75 Re	dB	-C							
76 Os	eB								
77 Ir	dB								
78 Pt	bB	-A							

Element \ Spectrum	I	II	III	IV	V	VI	VII	VIII	IX
79 Au	dA	dB							
80 Hg	aA	bA	eC	-D					
81 Tl	aA	cA	eC	eD					
82 Pb	aA	cA	eB	dB	dB				
83 Bi	eB	dC	eC	eC	eD	-B			
84 Po									
85 At									
86 Rn	bA								
87 Fr									
88 Ra	-A	dA							
89 Ac									
90 Th	-D	-A	-B	-B					
91 Pa									
92 U	-B	-B							
93 Np									
94 Pu									
95 Am									
96 Cm									
97 Bk									
98 Cf									
99									
100									

present state of knowledge of atomic spectra and the advances made since 1932.

We may divide atomic spectra into three main classes which have, however, many intermediates.

In the first place, there are the atoms where only one or two valence electrons contribute to the spectrum. Such spectra are usually characterized by Rydberg series. Their structure is simple and was recognized in most cases before the advent of the Bohr Theory (examples, Na and Ca). The second type is the multiplet spectrum of which the iron spectrum is a good representative. No progress was made in the analysis of such spectra until in the early twenties the theory of atomic structure had far enough advanced to serve as a reliable guide. These spectra are characterized by the fact that at least for the lower levels *LS* coupling holds so that Zeeman patterns can be used easily for the classification. The most probable transitions involve a much larger number of levels than of the first type, but they can be recognized as prominent multiplets. Most spectra of this type have now been analyzed with at least a fair degree of completeness although much detailed work remains to be done.

The third and most complicated type of atomic spectra is that found in the rare earths and the heaviest elements. Here the number of levels is so large that no particular multiplets are singled out. The spectrum consists, therefore, of an enormous number of lines, most of them of comparable intensity and without any apparent regularity whatsoever. Since no simple coupling scheme prevails, the interpretation of Zeeman data is difficult and no simple intensity and interval rules apply anywhere. This type of spectrum taxes the ingenuity and patience both of the experimental and theoretical spectroscopists. Our knowledge of these spectra is sketchy even in some of the most studied examples, and there are many cases where nothing at all is known about the structure.

The spectra of a number of elements are still completely unknown because these elements were not available in sufficient quantities. Recently some of these have been produced as fission products so that their spectra could be photographed.

The arc and spark spectra of 43 technetium, were produced recently by Meggers & Scribner (60) and 2,121 lines in Tc I and Tc II were measured. Previously only rough wavelengths of a few lines were known [Timma (76)]. The analysis of the Tc I and Tc II spectra, which are similar to the Mn spectra, has been carried out but not yet been published.

Similarly the spectrum of 61, promethium, was produced with 5 mg. of Pm^{147} by Meggers, Scribner & Bozman (61). This element occurs with an abundance of 2.6 per cent in the uranium fission products. Feldman & Timma (76) had previously recorded a few lines, but Meggers, Scribner & Bozman measured more than 2,200 lines of Pm I and Pm II. So far no attempts at a classification of the Pm spectrum have been made, which presents the difficulties typical of a rare-earth spectrum.

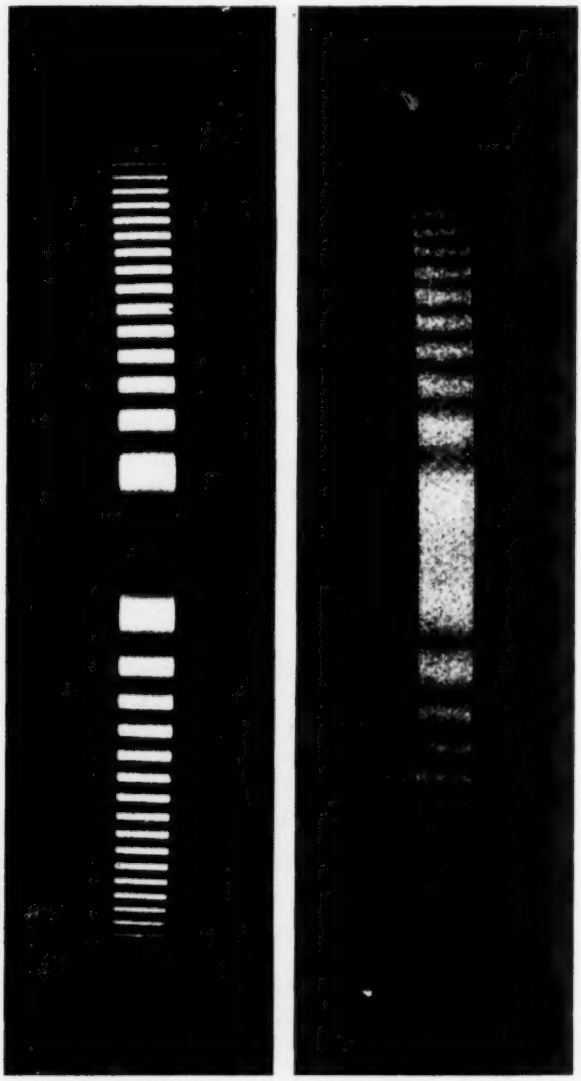

FIG. 8. Interference fringes of Hg^{198} (left) and Cd, showing difference in sharpness [from Meggers & Westfall (62)].

In the spectrum of mercury ($Z=80$) some new developments have occurred which deserve to be mentioned. It is well-known that the mercury lines have a complicated structure because of the fact that natural mercury has the following isotopes: Hg^{196} (0.15 per cent), Hg^{198} (10.1 per cent), Hg^{199} (17.0 per cent), Hg^{200} (23.3 per cent), Hg^{201} (13.2 per cent), Hg^{202} (29.6 per

cent), and Hg^{204} (6.7 per cent). In addition to the structure resulting from the different isotopic species, there is hyperfine structure for the isotopes with odd masses.

By irradiating Au^{197} with neutrons pure Hg^{198} has been obtained in considerable quantities. The lines of Hg^{198} are strictly single and, because of the heavy mass of mercury and the relatively low temperatures and pressures at which the spectrum can be produced, remarkably sharp. Meggers (57) proposed to replace the red cadmium line by the green line of Hg^{198} as primary standard of wavelength and eventually make it replace the standard meter as primary standard of length.

Several sets of measurements of Hg^{198} lines with respect to the present primary standard, the 6438.4696 Å line of cadmium, have been made (17, 18, 57, 62, 64) and are in excellent agreement. It was proposed to accept the preliminary value 5460.7532 Å for the wavelength of the primary standard. Meggers & Kessler (58) measured 20 other lines of Hg^{198} against this standard and found that the values are accurate to eight significant figures and that the probable error is in general less than 0.0001 Å. It turned out that insufficient knowledge of the index of refraction, particularly in the ultraviolet, is now the greatest uncertainty for obtaining reliable wave numbers and energy levels from these data.

Figure 8 shows how much sharper the Hg^{198} lines are than the red cadmium line.

Hg^{202} has been obtained with reasonable purity by electromagnetic separation from natural mercury, and Burns has measured the shifts between Hg^{202} and Hg^{198}. Its lines should be equally good as the Hg^{198} lines. Because of the relatively greater ease with which pure Hg^{198} can be obtained, it seems reasonable to assume that a line of Hg^{198} will eventually become the official international standard of length.

Heavy elements.—The information concerning the spectra of the heaviest elements is still extremely meager. The spectra of astatine-85, francium-87, polonium-84, berkelium-97, and of californium-98 are completely unknown. Analyses have been attempted only for thorium and uranium. The elements from actinium on constitute the second group of rare-earth-like elements where the 5*f* shell is filled in. The difficulties in the analyses of the structure of these spectra are, therefore, at least those of the rare-earth spectra. In addition, the rarity and radioactivity and high toxicity of most of these elements render it difficult to produce the spectra, so that a satisfactory description with accurate wavelengths is lacking in many cases.

89 Actinium: Only a few lines were known. The spectra have recently been successfully photographed by Fred & Tompkins; they are being measured and analyzed by Meggers.

90 Thorium: The spectrum of thorium is fairly well-known. A beginning has been made with the analysis of the Th I spectrum (45, 71). The Th II spectrum (25, 49, 50) has been analyzed rather completely. Recently

Klinkenberg (44) revised and extended the analysis of the Th III spectrum so that it is now also rather completely known and interpreted [see also Racah (66)]. Finally some lines have been classified in the Th IV spectrum (43).

91 Protactinium: The only work done on this spectrum [Tompkins & Fred (77)] lists 263 lines to an accuracy of 0.1 Å. No information is available on the state of ionization. The data are meant only for the identification of the element in spectrochemical analysis. Hyperfine structure is present.

92 Uranium: Much work has been done on the spectrum of uranium but the analysis is still incomplete. Kiess, Humphreys & Laun (38, 79) obtained new photographs of the spectrum, measured more than 9,000 lines, and classified about 2,000. Only the classified lines have been published. The spectrum of U II has been the subject of numerous investigations. Partial analyses have been given by a group of Dutch investigators (71, 72, 79, 81) and by McNally & Harrison (55). The Dutch group has published the classified lines and the energy levels; no details have so far been published by McNally & Harrison. The only place where unclassified lines can be found is in the M.I.T. wavelength tables which are far from complete. The classified lines of U II belong to two groups. Those of group A end on levels of the configuration $5f^47s$, those of group B on $5f^37s^2$, $5f^36d7s$, and $5f^36d^2$. So far no intercombinations have been observed and there is some difference of opinion on whether group A or group B has the higher energies (53, 80). Undoubtedly this will be cleared up by further research. Much may be expected for further classification from isotope shifts and possibly hyperfine structures.

93 Neptunium: The situation is similar to that for Protactinium. One hundred fourteen lines were observed by Tomkins & Fred (77), some with resolved hyperfine structure (see Fig. 15).

94 Plutonium: The spectrum was first photographed by Dodgen, Chrisney & Rollefson (26) with the copper spark method, and by Tomkins & Fred (77) with more or less the same technique (220 lines). The agreement between the two sets of measurements is reasonable with many apparent differences in relative intensities. There is no knowledge of the state of ionization or of isotope shifts or hyperfine structure.

95 Americium: 227 lines were observed by Tomkins & Fred (77). They were able to show by changes in discharge conditions that most, if not all, of these lines are due to ionized americium. They also showed that the americium spectrum is simpler than that of the neighboring elements and that it must be very similar in structure to the europium spectrum. No beginning, however, has been made with the actual analysis.

96 Curium: Some lines suitable for spectrochemical analysis have been reported by Conway, Moore & Crane (22).

One of the significant difficulties that confront anyone who wants to inform himself on the status of our knowledge of a particular spectrum is the unsatisfactory way most data are now accessible. The reason for this state of affairs is the fact that the gathering of accurate and complete experimental data for any but the simplest spectra is a fairly lengthy and complex affair. For many spectra the data go back to the time when demands on accuracy and completeness were not very high. From time to time more recent observers have gathered additional data necessary for a particular task of classification. In the more complex spectra it has become the habit to publish only the classified lines, forcing any subsequent worker who might be interested to carry the analysis further to start with photographing and measuring the whole spectrum anew even if his objectives are very limited. It is needless to say that this often results in discouragement at the outset, so that many tasks that should be undertaken in order to round out our knowledge of the spectra are never begun. Matters are made worse by the fact that most scientific journals are forced to refuse publication of spectroscopic material containing any lengthy wavelength tables.

In the earlier phases of spectroscopy the handicap of having the data widely scattered over the literature was overcome by the publication of summary reports like the well-known reports on series regularities by Fowler and by Paschen-Goetze, and particularly the monumental *Handbuch der Spectroscopie* by Kayser. The information contained in the eight volumes that have appeared is vast but mostly antiquated now and even the most recent volumes cannot fulfill the demands of a modern worker.

What is needed is a critical evaluation of the available data for each spectrum, preferably supplemented by new data where they are needed. It is a fact which, given the circumstances mentioned, is perhaps not too surprising that such a modern up-to-date critical review exists for not a single spectrum. It is quite evident that further progress in many branches of both atomic and molecular spectroscopy will be greatly retarded unless such data are available. It is not the place here to suggest possible remedies for this situation.

It is a matter of satisfaction that those spectroscopic data that are of most concern to the general scientific public are now adequately taken care of. The spectroscopist, after analyzing a spectrum, obtains from the empirical data the energy levels. A knowledge of these energy levels is the most important requirement for the elucidation of the details of atomic structure and for other applications. Bacher & Goudsmit in 1932 published their well-known compilation *Atomic Energy States as Derived from the Analysis of Optical Spectra*, which became the standard reference work for this subject. Because of the steady accumulation of new material this book gradually became out of date.

A new set of volumes published under the auspices of the National Bureau of Standards began to appear recently, *Atomic Energy Levels as*

Derived from the Analyses of Optical Spectra by Moore (63). These volumes contain all the known atomic energy levels (with the exclusion of those derived from typical x-ray data). Miss Moore has compiled not only all the data contained in the literature but through correspondence with spectroscopists all over the world has obtained much unpublished material. While no actual measurements of lines are given, the references make the location of the original data much easier. Volume I containing elements 1(H) to 23(V) appeared in 1949. Volume II with elements 24(Cr) to 41(Nb) is about to come out, and the other volumes are to appear when the data have been compiled.

For this compilation which is much more than a routine job, Miss Moore deserves the thanks not only of all spectroscopists but of all scientists who have occasion to use spectroscopic data.

Isotopic Shifts in Atoms with More Than One Electron

As early as 1918 there was evidence that there were small shifts between the atomic lines of different isotopes of the same element. Because of the smallness of the shifts, data were difficult to obtain as long as only the naturally occurring isotopic mixtures were available, and the data were not sufficient for an adequate interpretation of such shifts. Since the war, when separated isotopes became available on a larger scale, data have been accumulating fast and considerable progress has been made in the understanding of such effects. The many new isotopes that became available through irradiation of elements or as fission products are helping a great deal (examples, T, He^3, Hg^{198}, etc.).

When the growing accumulation of data the interpretation of the isotope shift has also made progress although some features are still imperfectly understood.

We can separate the nuclear properties into two general classes: (*a*) effect of finite mass, and (*b*) effect of departures from Coulomb field.

Effect of finite mass.—We regard the nucleus still as a point charge but having a finite mass M so that it will move about the center of gravity of the atom. The simplest case beyond that of the hydrogen atom (see section on One-Electron Spectra) is that of two extranuclear electrons. This problem has been treated theoretically by Hughes & Eckart (99).

The shifts resulting from the finite mass of the nucleus can be separated into several parts. By replacing the mass of the electron in the Rydberg constant by the reduced mass μ, all energy levels are multiplied by a factor $\mu/m=[1+(m/M)]^{-1}$ or they are shifted by the fraction $-m/M$ of their energy. This is called the elementary mass shift (see section on One-Electron Spectra). For unit mass differences this shift decreases with the square of the atomic weight. For a line at 5000 Å it is about 0.01 Å for $M=16$ and becomes negligibly small for higher masses.

The elementary mass shift is not the only shift because the motion of the individual electrons is not independent. In order to calculate the specific

mass shift which is the difference between the total shift and the elementary shift a knowledge of the wave function is necessary.

For two electrons the effect can be understood without any great difficulty. If two electrons would move in such a way that they always are exactly opposite each other with respect to the nucleus, the latter would remain at rest and there would be no mass effect at all. This means that the specific effect would be equal to the elementary mass effect and of opposite sign. The other extreme would be if the two electrons would move together, in which case the change would be as if the electron had the mass $2m$. Again the elementary and specific mass effects are equal but this time they have the same sign. The actual situation will be in between the extreme cases. If the two electrons move completely independently of each other the specific effect is zero.

For a two-electron atom the specific effect can be further analyzed and separated into two parts of different significance.

The first part results from the fact that two electrons cannot move independently of each other because of the Pauli exclusion principle. It can be easily shown (99) that only the P levels are affected by this and that for the

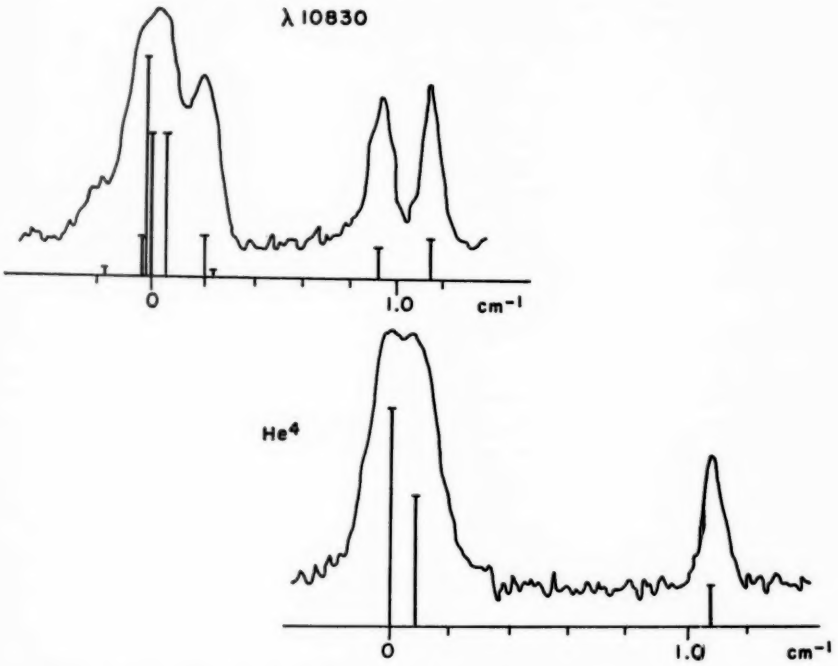

FIG. 9. The 10830 line of He^3 and He^4. Microphotometer trace of interferometer patterns. The vertical lines give the calculated positions and intensities of the fine and hyperfine structure components [Fred & Tompkins (98)].

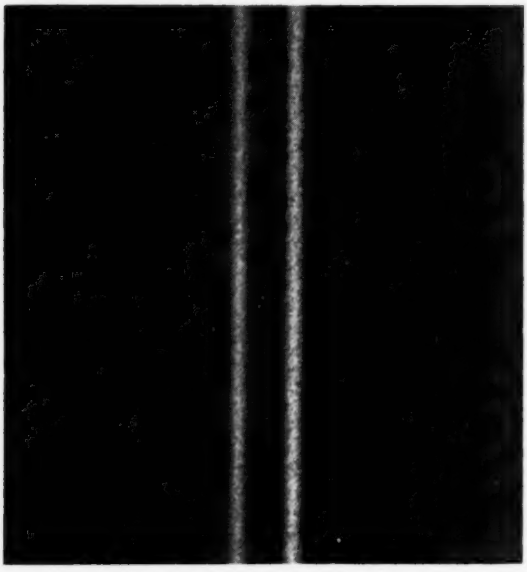

FIG. 10. Isotope shift in the singlet line 5016 Å of helium separation 0.85 cm.$^{-1}$ (Byrne, Johns Hopkins University).

singlet terms the two electrons are more often on the same side of the nucleus, for the triplet terms more often on opposite sides. This means that for the singlets the nucleus will move more violently than for independent electrons. The total mass shift will, therefore, be larger than for independent electrons; for the triplets it will be just the other way around.

Hughes & Eckart calculated an approximate expression for this exchange mass correction for the *np* levels. The specific effect must, of course, disappear at the ionization limit.

The other effect is called polarization effect. It results from the fact that because of the electrostatic interaction the electrons push each other away and tend, therefore, to be on opposite sides of the nucleus. This polarization effect tends to diminish the motion of the nuclei and acts, therefore, in the opposite direction as the elementary mass effect.

It is clear that all these mass effects are appreciable only for light nuclei. They have been studied recently quite extensively for He^3 and He^4 by Tomkins, Fred, Brody & Hammermesh (98).

The shifts between He^3 and He^4 were determined by accurate interferometric measurements with the conditions of the discharge carefully controlled so as to give lines of maximum sharpness. The analysis is complicated by the partly resolved hyperfine structure of He^3, which is of the same order of magnitude as the narrow fine structure of the triplet lines. The helium spectrum is now the only spectrum on which mass shifts have been measured with any degree of completeness.

Table II gives a summary of the results. In the third column the measured

TABLE II

ISOTOPIC SHIFTS IN THE SPECTRUM OF HE I

Line	λ	$\Delta\nu$	$\Delta\nu_{el}$	$\Delta\nu_{sp}$
2^3P-3^3S	7065	−0.036	0.634	.670
4	4713	+0.297	.951	.654
5	4120	0.438	1.087	.649
6	3867	0.508	1.159	.651
7	3732	0.548*	1.209	.661
8	3652	0.586*	1.227	.641
2^3P-3^3D	5875	0.123	.763	.640
4	4471	0.360	1.113	.639
5	4026	0.474	1.113	.639
6	3819	0.547	1.713	.626
7	3705	0.592	1.210	.618
8	3634	0.617*	1.233	.616
2^3S-2^3P	10830	1.151	.414	−.737
3	3888	1.404	1.153	−.251
4	3187	1.535*	1.406	−.129
2^1P-3^1S	7281	1.046	.615	−.431
4	5047	1.333	.888	−.445
5	4437	1.461	1.010	−.451
6	4168	1.529	1.075	−.454
7	4023		1.113	
8	3935	1.606*	1.138	−.468
2^1P-3^1D	6678	1.124	.671	−.453
4	4921	1.358	.910	−.448
5	4387	1.462	1.021	−.441
6	4143	1.512	1.081	−.431
7	4009	1.532	1.118	−.424
8	3926	1.543*	1.141	−.402
2^1S-3^1P	5015	0.849	.888	0.039
4	3964	1.165	1.130	−0.035
5	3613	1.304	1.240	−.064
6	3447	1.344*	1.300	−.044
7	3354	1.375*	1.336	−.039

* Taken at higher gas pressure. Results probably less accurate.

shifts are given. Wherever there is hyperfine structure in He^3 the values are the difference between He^4 and the center of gravity of the He^3 pattern. Column 4 ($\Delta\nu_{el}$) gives the shifts that the line would undergo, if only the elementary mass effect were operating. The next column ($\Delta\nu_{sp}$) gives the difference between Column 5 and 3 and represents the observed specific mass effect.

The specific effect as we have seen represents the coupling between the two electrons, and it can approximately be split up into two parts, the exchange mass correction and the polarization effect.

The former may be positive or negative and may be of the same order of magnitude as the elementary effect for a particular energy level but must be numerically smaller. It is different from zero only for the P levels.

The polarization effect which represents the effect due to the excited electron pushing the other electron away is always of the opposite sign as the elementary effect and numerically much smaller.

Let us examine first the 2^3P-n^3S series. The specific shift is approximately constant, the average being 0.644, which must be the specific shift for the 2^3P state. The deviations from a constant amount can only be explained as shifts in the initial levels. The variation, however, does not follow any specific trend and may possibly be a result of experimental errors, even though the maximum deviation from the average (0.016) exceed the statistical errors by a factor of two or three. Because of the unresolved fine structure the measurements are difficult and possibly most of the variation can be attributed to experimental errors. Similarly the shift in the 2^1P level is ± 0.450.

These empirical shifts -0.644 and $+0.450$ compare to theoretical values -0.565 and $+0.372$ calculated from Hughes & Eckart's formula (99). The discrepancy ± 0.08 for both cases is not large but definitely outside the experimental errors. It cannot be accounted for by the polarization effect in the $2P$ state because this should be negative in both cases. It is not unreasonable to expect that the discrepancy results from the fact that extremely crude wave functions were used in deriving the formula and that if this calculation were made with the proper wave function the discrepancies would disappear.

Going now to the 2^3S-2^3P line we find as the shift of 2^3S, $+0.13$. In the approximate theory the only shift to be expected for an S state is that resulting from polarization which should have the opposite sign. This shows again that the theory in its approximate form cannot give an accurate quantitative account of the shifts. With the 2^3S shift known the shifts of 3^3P and 4^3P can be obtained as 0.128 and 0.006. These agree as far as order of magnitude is concerned with the calculated values.

The result of the very complete analysis of the helium shifts shows that the simple theory of mass shifts accounts satisfactorily for the general trend of the shifts. That it does not predict quantitatively all details is not surprising considering the crude assumptions that were made.

Structure effects.—For heavy elements the magnitude of the mass shifts are insignificant and the isotope effects are structure effects. The methods

that have to be employed when only the natural isotopic mixture is available and the results that can be obtained notwithstanding the handicap can be shown well with the example of samarium (88, 91).

Natural samarium, a rare earth with $Z=62$, consists of seven isotopes with mass numbers (and abundances) as follows: 144 (27.0 per cent), 154 (14.8 per cent), 148 (11.1 per cent), 149 (13.7 per cent), 150 (7.4 per cent), 152 (27.0 per cent), 154 (22.9 per cent). A number of lines in the Sm I and Sm II spectrum show resolvable structure. With a grating they appear as doublets, with the highest obtainable resolution (Fabry & Perot interferometer) as shown in Figure 11. This figure was obtained from the microphotom-

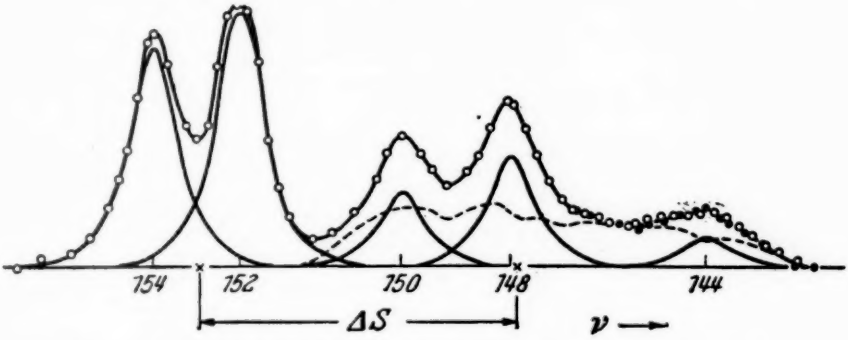

FIG. 11. Analysis of the observed isotopic and hyperfine structure of the 6589 Å line of samarium [Brix & Kopfermann (91)].

eter trace of the interferometer plate by converting the densities to intensity values with the help of a proper plate calibration. This furnishes the experimental curve indicated by the circles. It shows five maxima which are attributed to the five even isotopes as the two odd isotopes have hyperfine structure and, therefore, may be expected to have an unresolved broadened pattern without sharp maxima. The left pair belonging to Sm^{154} and Sm^{152} is practically free from overlapping by the other isotopes. It can be resolved into two components with the intensity ratio 22.9:27.0 of the abundances. The curves for the other three even isotopes can then be drawn with the maxima at the place of the observed maxima, the shape the same as that of Sm^{154} and the area proportional to the respective abundances. The five curves for the even isotopes are then subtracted from the experimental curve and what remains (dotted in Fig. 11) must be a result of the two odd isotopes. An attempt is then made to represent the dotted curve as a superposition of two curves. The knowledge that the center of gravity of the intensity distribution of a line remains independent of the hyperfine structure helps but there would hardly be a unique result with the data of Figure 11. Other lines which have nearly a negligible hyperfine structure are more favorable.

The result of the analysis is given in Figure 12 where the numbers are the

numbers referred to, the separation ΔS between the center of gravity of the five left components on the one hand and that of the two components at the right on the other hand, taken as unity. All lines when represented in this fashion have the same structure within the limits of experimental errors. The experimental value of ΔS for the line 5979.38 of Figure 12 is 0.150 cm.$^{-1}$.

The analysis just sketched can be carried out only for those lines that show the largest shifts and which, moreover, are free from other lines of different origin which would confuse the picture. Brix & Kopfermann (91) could find only five such Sm I lines. They found, however, many other lines

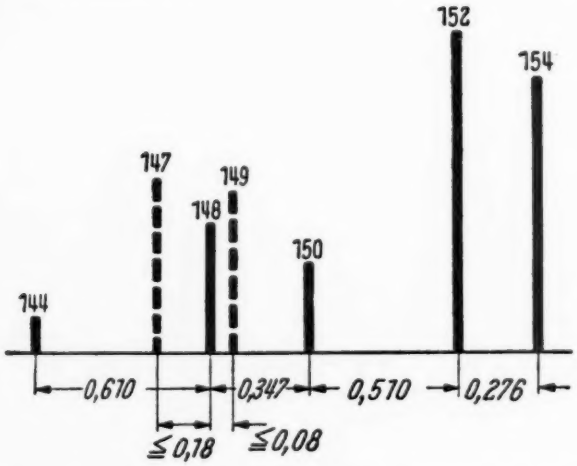

FIG. 12. Isotopic structure of a samarium line. The separations are given in terms of ΔS (see Fig. 11) [Brix & Kopfermann (91)].

which showed noticeable isotopic shifts which are, however, less well measured.

The normal state of Sm I has the configuration $4f^6 6s^2(^7F)$ and the prominent classified lines with the large isotope separation are due to transitions to this level from the $4f^6 6s 6p$ configuration. The observed shifts are, therefore, due to the difference in the shift between a $6s$ and a $6p$ electron.

It is apparent that a proper study of the isotope shifts under such conditions as described for samarium is greatly handicapped by the complexity of the pattern. This results from the large number of isotopes and the fact that some show hyperfine structure. A very accurate determination of the shift pattern given in Figure 11 cannot be expected; moreover, the procedure of obtaining the results is very laborious. There are many cases where the situation is even more unfavorable than that given for samarium.

The solution for most of the difficulties is to work with only one isotope at a time instead of the natural mixture. This was impossible not so long ago, but now in many cases separated or partly separated isotopes are avail-

able. If such isotopes are used the interpretation of the results is greatly simplified. The source of the isotopes is electromagnetic separation, transformation by neutron irradiation, or fission products. In some cases the quantities available are small, but often no more than a few micrograms are needed in order to obtain the spectrum containing the principal lines. In some cases sufficiently large quantities may be obtained for elaborate spectroscopic experiments (e.g., He^3, Hg^{198}, U^{235}).

Before World War II there were only very few cases where it had been possible to obtain isotopic shifts and hyperfine structure from separated isotopes. The Atomic Energy program has provided opportunities on an increasing scale for experiments with separated isotopes. The results of such

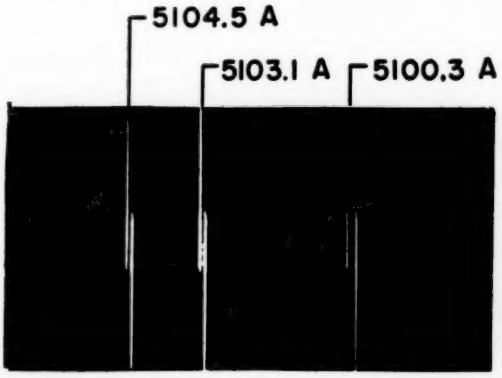

FIG. 13. Grating spectra of Sm^{144} and Sm^{154} [Smith & McNally (106)].

spectroscopic work are now coming out in the literature. It may be expected that this is only the beginning and that in a few more years our knowledge of isotopic shifts and hyperfine structure and the information concerning the structure of the nucleus resulting from such data will have greatly increased.

Figure 13 shows the results of Smith & McNally (106) for some Sm lines. The upper part represents Sm^{144}, the lower Sm^{154}. The shifts are now easily measured and interpreted. More than 400 shifts were measured. The results can now be used for the classification of the samarium lines. Another important example is uranium. Here large quantities of the naturally occurring isotopes 238 and 235 can be obtained, as well as some of the less frequent and artificial isotopes (see Fig. 14).

Further recent examples of isotope shifts will be found in the bibliography. More significant results may be expected for many additional elements through the increasing availability of separated isotopes.

The general features of most of the results so far obtained are that the lines resulting from the even isotopes which show no hyperfine structure are spaced nearly equidistantly. The centers of gravity of the odd isotopes are also spaced equidistantly but shifted with respect to the even isotopes. This

staggering effect was discovered quite early. It is very pronounced in uranium (see Fig. 14).

The reason for the isotopic shifts in heavy elements has nothing to do with mass differences of the nuclei. Deviations from the strict Coulomb field because of the fact that the nucleus does not represent a point charge are responsible for the differences.

The field of any charge distributions can be represented by a series of electric and magnetic poles of increasing order. The leading term is the electric monopole equal to the nuclear charge. Because the spacing of nuclear energy levels is very large compared to the energies of the external electrons,

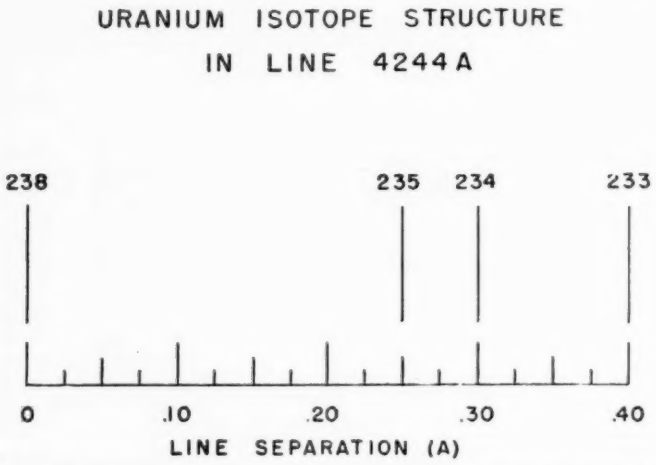

FIG. 14. Isotopic structure of the 4244 Å line of U II (McNally).

only the average values of the multipoles are of importance. This means that the magnetic dipole and the electric quadrupole are next in importance. The series converges very well for distances which are large compared to nuclear dimensions.

In an actual atom the wave function of the external electrons is not negligible in many cases even very close to the nucleus so that the multipole expansion may not be quite sufficient.

It has been found that a model which regards the nucleus as a rigid sphere of finite radius is able to give account of the principal features of the isotope shift, namely the regular spacing and the order of magnitude of the separation. The field is a Coulomb field outside the sphere and the potential regarded as constant inside it. The radius of the sphere increases regularly with the mass number.

In order to understand unequal spacings Breit, Arfken & Clendenin (115) considered polarization of the nucleus by the electron and found that this might account for some of the phenomena without excluding the possibility of other explanations. The so-called Schmidt model, which considers the

nucleus as consisting of a core without a magnetic moment and a single nucleon outside it, has been shown to give an explanation of the odd-even staggering (Fierz, Kopfermann, Breit). These features of the nucleus have become of particular interest since the shell theory of the nucleus has been developed (134).

Hyperfine Structure

With high resolution many atomic lines show hyperfine structure resulting principally from the presence of a nuclear angular momentum I and a magnetic moment m. The results up to 1940 are presented in the monograph by Kopfermann (127). A listing of all known nuclear spins, magnetic moments, and electric quadrupole moments was given by Mack (130). It is complete up to the beginning of 1950 and contains a detailed bibliography. The value of the nuclear angular momentum is essentially determined from the observed number of components, the magnetic moment from the magnitude of the splitting, and the quadrupole moment from the distortion of the regular pattern. Intensities are also helpful for the interpretation. The study of hyperfine structure represents the classical method of obtaining nuclear data from spectroscopic measurements and the techniques have been well worked out before. The bibliography will show the progress during 1950. Some notable new hyperfine structures are technicium and neptunium (Figure 15).

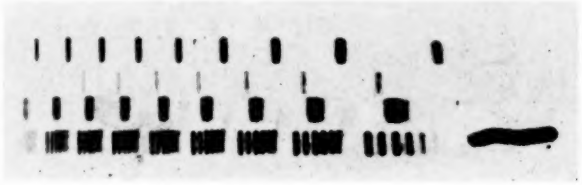

Fig. 15. Hyperfine structure of neptunium [Tompkins (108)].

The availability of separated isotopes has made the collection and interpretation of data considerably more satisfactory in many cases. Significant results can be obtained with very small quantities of material.

The microwave and radio-frequency measurements in recent years have significantly supplemented the hyperfine structure data (see sections on Microwave Spectra and on Radio-Frequency Spectroscopy). For the interpretation of the results see the chapters on "Recent Developments in the Theory of Nuclear Structure" and "Nuclear Moments" in this volume.

Diatomic Molecules

The spectra of molecules are affected by the properties of the nucleus in various ways. In the first place there are direct mass effects. In addition there is the influence of other properties of the nucleus such as spin or quadrupole moments, symmetry properties, etc.

In this section we shall confine ourselves to those properties that can be observed in the spectra in the ultraviolet, visible, or near infrared. Microwave spectra where much finer details of structure can be resolved will be dealt with in the next section.

The hyperfine structure due to the interaction of the nuclear spin with the electronic angular momentum is too small in almost all cases to be observed. One clear case of such interaction was observed recently in He_2. Small isotope shifts resulting from differences in the nuclear field even if large enough to be observable would be masked by the much larger mass shifts in the vibrational and rotational energies.

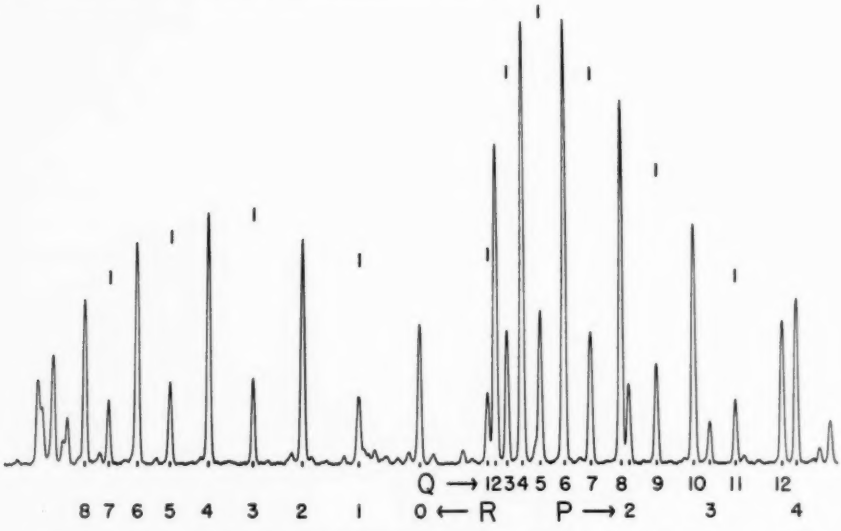

FIG. 16. Photoelectric trace of the He^3_2 band at 4650 Å. The short vertical lines represent the length of the weak lines multiplied by three. This proves the nuclear spin of He^3 to be 1/2 [Dieke & Robinson (156)].

One effect resulting from the influence of nuclear properties for which there is no analogue in atomic spectra is that the total wave function for homonuclear molecules must be antisymmetric or symmetric in the nuclei, depending on whether the number of nucleons in each nucleus is odd or even. From this follow the well-known intensity alternations of successive rotational lines in the ratio $(I+1)/I$ when I is the nuclear spin. These ratios may be measured empirically and used for the determination of the nuclear spin of a particular isotope. It is well-known that the nuclear spins of most of the light elements were originally determined by this method.

Recently this method has been used to determine the nuclear spins of tritium (157) and He^3 (156, 159). Figure 16 shows the actual intensities in a He^3_2 band with the $(I+1):I$ ratio equal to 3:1. It is clear that, for moderate

values of I, at least, the intensity measurements need not be very accurate to discriminate between the various possible spin values.

The molecular spectrum of hydrogen has a particular place among the molecular spectra because H_2 is the simplest of all molecules. It may be hoped, therefore, to obtain a complete theoretical treatment of all its details. Such details which cannot be quantitatively treated in the heavier molecules can then at least be understood by analogy with the corresponding situation in the H_2 molecule. Paradoxically, the empirical structure in the H_2 spectrum appears to be at first sight much more complicated than for almost any other diatomic molecule. No bands or any other immediately apparent regularities stand out. The reason for this is the fact that the rotational structure is so wide that between successive rotational lines of one band there are usually many lines as a result of different electronic and vibrational transitions which confuse the structure. Moreover, interactions between electronic motion and rotation or vibration are particularly prominent because of the light nuclei and cause many irregularities which also confuse the structure.

For these reasons it is particularly fortunate that the hydrogen molecule exists now in the following six species with the reduced masses indicated in parentheses: $H_2(0.50)$, DH(0.67), $D_2(1.00)$, TH(0.75), TD(1.20), and $T_2(1.50)$. This makes it possible to study, actually, properties of the molecule as function of the reduced mass. Furthermore, dubious regularities in one species can be tested by comparing them with the same structure in the other molecules. Finally, considerably more accurate values of the molecular constants may be obtained. For example, the vibrational energy is given by the formula

$$E_V = Y_{00} + Y_{10}(V + \tfrac{1}{2}) + Y_{20}(V + \tfrac{1}{2})^2 + Y_{30}(V + \tfrac{1}{2})^3 + \cdots \qquad 1.$$

when the Y_{lm} are constants which depend on the potential energy as well as on the reduced mass.

For a light molecule such as H_2 the expression 1 converges very poorly. In order to have a good approximation a considerable number of terms should be used. For instance, in order to find all the Y_{lm} up to Y_{60} from the empirical data, all vibrational levels up to $V=6$ must be used. The larger V is, however, the poorer is the convergence of 1. This poses a dilemma for which there is no easy way out, if we restrict ourselves to H_2 alone.

The Y_{lm} depend on the reduced mass in a known manner. By making use of all six isotopic species we can obtain the constants up to Y_{60} without using vibrational levels beyond $V=1$. The convergence will be adequate and the constants so obtained are more accurate and can be used to find a reliable potential energy curve.

A great deal of work was devoted between 1920 and 1940 by many investigators on the elucidation of the structure of the H_2 spectrum. Sir Owen Richardson with his collaborators was perhaps the most successful and the main features of this complicated spectrum became clear. Nevertheless, many lines remained unclassified, some of the regularities found seemed dubious, and difficulties arose in the interpretation of others. The availability of

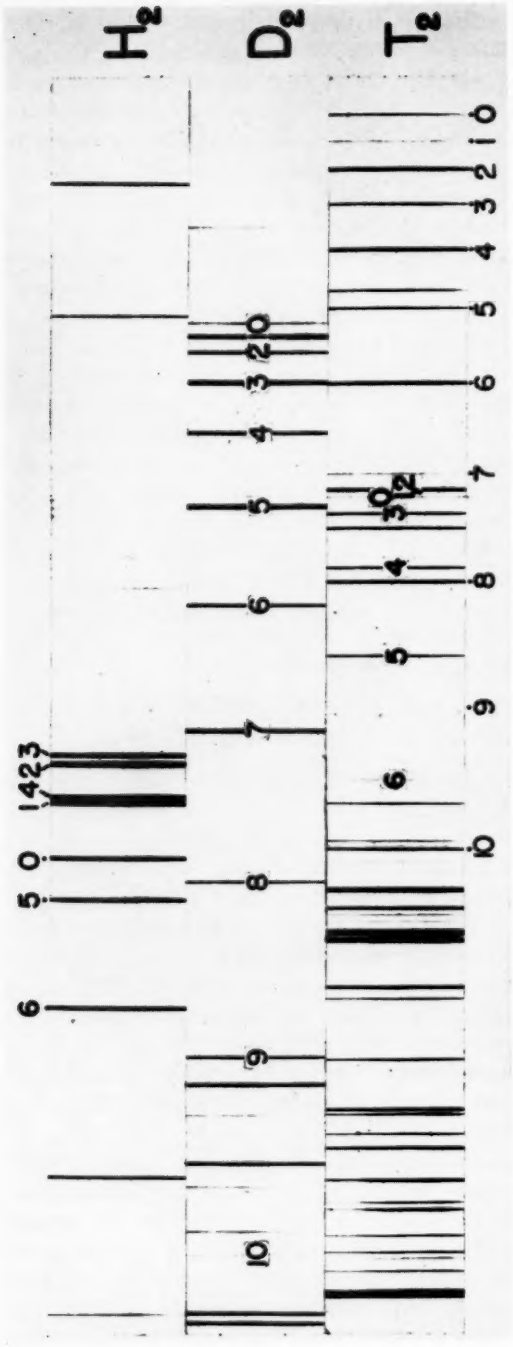

FIG. 17. Comparison of the same band (near 4650 Å) in H_2, D_2, and T_2. Note that more than a change in scale is involved in the change. On the lower spectrum also the TH band shows (Johns Hopkins University).

the DH and D_2 spectra through the discovery of deuterium helped to get over some of the difficulties. The possibility of studying now all six isotopic species is removing most of the remaining uncertainties.

The spectra of H_2, D_2, and T_2 can be obtained pure. Under optimum conditions in a discharge tube only 50 per cent of the molecules present can be DH, TH, or TD, the rest being H_2, D_2, or T_2. For this reason the spectra of the mixed molecules cannot be obtained with the same completeness as those of the homonuclear molecules.

At the present time the spectra of TH and T_2 have been photographed and measured with great completeness (157, 158) except in the vacuum ultraviolet. The TD spectrum will be obtained as soon as very high purity tritium becomes available for this purpose. The question of the purity of tritium is not so much a matter of preparing some pure sample but getting it into a discharge tube and keeping it free from ordinary hydrogen under severe conditions of a heavy electrical discharge. All other impurities but hydrogen can be easily removed. The contamination by hydrogen is serious because it is given off in appreciable quantities from electrodes and the glass or quartz walls of the tube even after careful outgassing when an electrical discharge is applied. The spectra so far obtained show about 90 per cent T_2, 10 per cent TH, and traces of H_2, but it is fairly certain that without too serious difficulties it will be possible to obtain a 99 per cent T_2 spectrum, where the TH impurities will be of no consequence.

In many respects the T_2 spectrum is better suited for a detailed analysis than the H_2 spectrum, as the bands are more easily recognizable because of the closer spacing of the lines and the irregularities resulting from interactions are smaller. All the principal band systems have been found and those which have been analyzed in detail are believed to be considerably better known now for T_2 than for H_2.

Another spectrum where the availability of a new isotope provides a great deal of help for the analysis is that of diatomic He_2. Such molecules are formed in a discharge tube particularly if the pressure is fairly high. The molecule persists long enough to emit an extensive band spectrum throughout the visible and the adjacent parts of the ultraviolet and infrared. There are many different electronic states involved which show perfectly normal bonding. Through long Rydberg series (up to eight members, the longest observed in any molecular spectrum) the constants of the He_2^+ ion can be determined with considerable accuracy. Parts of the spectrum show complicated interactions but there is enough resolution so that details may be studied.

He^3 can be obtained in pure form and completely free from He^4 from the decay of tritium. The 6400 band of He^3_2 was analyzed by Douglas & Herzberg (159) and from it the nuclear spin of He^3 determined as 1/2. The whole He^3_2 spectrum was photographed completely at the Johns Hopkins University, with better dispersion than had been employed in the past for the He^4_2 spectrum, and analyzed (156).

Isotopic substitutions in other diatomic and particularly polyatomic molecules are used extensively for the elucidation of complicated structures. In particular the substitution of deuterium for hydrogen in polyatomic molecules has proved very fruitful. Even a complete bibliography of this subject would exceed the bounds of this report. Attention is drawn, therefore, to the review articles by Halverson (161) and the bibliography by Kimball (163).

Microwave Spectra

The techniques for producing and measuring very short radio waves were developed to a high degree of perfection during the war for radar devices. This same technique was very useful for obtaining spectroscopic data. Something had been done in this field before the war, but the techniques were clumsy and relatively little progress was made.

At the present time it is not too difficult to handle waves down to about 2.5 mm. wavelength, which is equivalent to frequencies below 120,000 megacycles or wave numbers below 4 $cm.^{-1}$. The region thus accessible contains the rotational frequencies of all but the lightest molecules. During the study of such rotational transitions it turned out that most of the lines displayed fine structure or as it better should be called, hyperfine structure, as this structure results from properties of the nucleus.

Before reporting any details of microwave spectra a brief comparison should be made between the type of data and their accuracy that can be obtained through microwave spectroscopy with similar data obtained from the older methods of ultraviolet, visible, and infrared spectroscopy.

The rotational frequencies may often be obtained in the visible or near infrared combined with electronic or vibrational frequencies. This means that the rotational frequency is obtained only as a small difference between very large numbers. The consequence of this is that although the accuracy of measurement in the visible is very high, the relative accuracy of the small differences may be quite poor. In the microwave region, on the other hand, even though the relative accuracy of the measurements does not quite equal that of visible spectroscopy, the rotational frequency is measured directly and this quantity can, therefore, be obtained with a much higher accuracy. An accuracy of one part in 2×10^6 is considered quite good for wavelength measurements on ordinary grating plates. Near 5000 Å this would give an accuracy of 0.01 $cm.^{-1}$ in the wave numbers. A rotational frequency of one wave number can, therefore, be obtained with that accuracy (0.01 $cm.^{-1}$) which means that it can be measured to 1 per cent. If this frequency is measured directly in the one centimeter region, it can be obtained without too much trouble with an accuracy of one part in two million which here, however, is the accuracy of the desired quantity itself.

This consideration applies, of course, equally well to rotational frequencies and other frequencies which show up in the visible only as fine structure of the lines. For such small frequencies the microwave measurements are vastly more accurate. Nor is this only a question of measuring technique.

Even if the interferometer is used which increases the accuracy roughly by a factor ten over that of grating measurements or if some vastly superior as yet uninvented instrument could be used by which wavelength measurements in principle could be made to any accuracy, there would not be much change in the situation as the limitations would then be imposed by the finite width of the lines themselves. The natural line width, that is, the width of the line when such broadening influences as Doppler effect or disturbance by neighboring atoms are entirely absent, is very much larger in the visible than in the microwave region. This explains the possibility of making much more accurate measurements (expressed in wave numbers) and resolving much finer structures than is possible in the visible.

In order to achieve this high resolution it is necessary to eliminate as much as possible all influences that tend to broaden the lines. This means that the gasses must be used at very low pressures and low temperatures.

In principle the type of measurements in the microwave region are not different from any other type of spectroscopic measurements, but the peculiarities in the technique of producing and receiving microwaves have necessitated many changes so that the actual procedure is very different from that used in ordinary spectroscopy.

This section deals only with straightforward microwave absorption methods. The radio-frequency methods will be taken up in the next section. It is obvious that emission spectroscopy is impossible in this region because of the small intensity of any emission line that possibly could be obtained. One reason for this is that the ratio of absorption to emission probability is proportional to ν^3.

A wave guide serves as absorption vessel and can be made as long as desired. This means that there is appreciable absorption even at the very low pressures of the gas (10^{-5} mm. of Hg is not uncommon) which are necessary for sharp lines. The waves are generated by methods familiar from radar techniques, usually by a reflection klystron. There is an essential difference with absorption spectroscopy at the shorter wavelength in that a continuous spectrum cannot be produced. The energy is highly monochromatic but can be continuously varied so as to sweep a particular absorption line. For this reason no spectrograph is necessary, that is, an instrument which disperses the radiation into its monochromatic components. The frequency is measured to an accuracy of one part in 10^4 with a cavity wave meter. When frequency standards are available the accuracy can be increased 100-fold.

The radiation, after having passed through the absorption wave guide, is measured by a crystal detector or by beating it against a standard frequency and measuring the difference by standard short wave radio-frequency methods. Bolometers and thermocouples also have been used.

A general account of the methods and results of microwave spectroscopy was given in 1948 by Gordy (187). A more recent compilation of results was presented in *Molecular Microwave Spectra Tables* by Kisliuk & Townes (196). This table contains published and unpublished results available February,

1949, and is to be brought up to date by future supplements. The bibliography will give an indication of some of the recent developments. Microwave spectroscopy is a very active field and new results are coming out rapidly. For nuclear physics the information about nuclear quadrupole moments which can be obtained from the fine structure of the rotational lines is of particular interest.

Radio-Frequency Spectroscopy

At wavelengths which exceed considerably the dimensions of the apparatus, where wave guides and resonant cavities become impractical, the methods of ordinary microwave spectroscopy are not usable. The methods used for such frequencies have techniques that are even more remote from ordinary spectroscopic techniques than those of microwave spectroscopy, although the type of result is in principle the same.

The methods are absorption methods; that is, transitions are induced in the atoms or molecules by oscillating magnetic or electric fields. Instead of observing the weakening of the electromagnetic field when it interacts with the molecules, as is done in ordinary absorption spectroscopy, the molecules that have undergone transitions are directly observed. The methods used for this are adapted to the particular problem.

Rabi and his collaborators (259) have in particular developed the magnetic resonance method when applied to molecular beams (242).

Transitions between the hyperfine structure components in a magnetic field give the nuclear magnetic moments. The method is similar to that described in the section on One-Electron Spectra for the Lamb-Retherford experiments, but of course antedates those experiments. Suitable molecules with relatively simple structure are usually used for this method. In these experiments the presence of strong nuclear electric quadrupole moments was first found.

More recently the electrical analogue of the magnetic resonance method has been developed (254, 256) which causes transitions in an oscillating electric field between the Stark components of a particular rotational level [Hughes (254), Trischka (293)]. Electric dipole moments, moments of inertia, and quadrupole interactions can be determined with high accuracy.

After earlier attempts with questionable success, radio-frequency resonance methods have been applied since 1946 to matter of ordinary density, such as liquids and solids as well as gases, for the study of nuclear properties. This means a great simplification in the experimental technique as the production of molecular beams and the measurement of their properties can be avoided. Two methods which have several features in common but differ in others have been chiefly used.

The nuclear induction method of Bloch (232, 233) forces the nuclear magnetic moment to precess about a constant field by placing the substance in a radio-frequency field in resonance with the nuclear Larmor frequencies.

The constant field is used as in the experiments previously described to bring the Zeeman transitions into the radio-frequency range. The radio-frequency change in magnetization caused by the Larmor precession is observed through an induced radio-frequency voltage.

The method of nuclear induction makes it possible to compare with great accuracy nuclear magnetic moments, as, for instance, those of the neutron, the proton (234, 243, 288), the deuteron (226, 267, 268, 284) and triton, and others, by measuring the resonance frequencies. Special detectors which are necessary for molecular beam experiments are not required. While in first approximation the nuclei behave as if they were independent of each other and of the neighboring molecules, this is not exactly true and thus interactions resulting from the liquid or solid state (278) may be studied as well as the process by which thermal equilibrium is established (236). Many other applications have already presented themselves or may be expected for the future.

Most of these statements are also true for the other method called the nuclear magnetic resonance absorption method, first introduced by Purcell, Torrey & Pound (281) though previously tried unsuccessfully by Gorter & Broer (246). The chief difference with the nuclear induction method is that resonance is observed by a reaction on the radio-frequency circuit which, for instance, throws a bridge off balance. A detailed review of this method has been given by Pake (273) to which the reader is referred.

Frequencies from a few megacycles to several thousand are useful for these methods (100 m. to 10 cm.).

In most of the radio-frequency absorption measurements the resonance frequencies of several substances are compared under otherwise identical conditions. This means that the nuclear magnetic moment of a particular substance is determined in terms of the nuclear moment of the comparison substance and no measurement of the magnetic field is required.

If the magnetic field is known accurately, the nuclear moment can be measured in absolute units, and such a measurement was recently made for the proton by Thomas, Driscoll & Hipple (289). Bloch & Jeffries (234), on the other hand, by comparing the frequency of orbital rotation of a proton in the magnetic field of a small cyclotron with the nuclear induction frequency, measured the magnetic moment of the proton directly in nuclear magnetons. Gardner & Purcell (243), by comparing the proton induction frequency with the cyclotron frequency of an electron, measured the proton moment in Bohr magnetons.

The radio-frequency method in any of the three forms mentioned in this section has proved to be capable of giving highly accurate important results. The proof that the gyromagnetic ratio of the electron is not exactly $e/2mc$ as derived by the simple theory is one of those results (265). The nuclear induction method and the magnetic absorption method which work with liquids and solids have already made important contributions to the knowledge of the structure of the solid state and the magnetic properties of matter.

Spectra of Liquids and Solids

The spectra of gases and vapors essentially yield the properties of free atoms or molecules. Interactions between the molecules manifest themselves only in relatively small effects as line broadening and frequency shifts unless extreme conditions prevail. On the other hand, where the molecules are as crowded together as they are in liquids and solids, the interactions play a prominent part. They usually broaden the lines so much that all structure disappears. Not much information can be obtained from such spectra.

There are cases where the motion from which a particular spectrum line results is relatively well-protected from the disturbance by neighboring molecules. The line may then be broadened but the frequency is still clearly recognizable. The molecular vibrations in organic molecules present examples for this. The infrared vibration frequencies can be observed with relative ease even though the substance is in liquid form.

Other examples are furnished by the inner electron shells of the elements in the iron group and particularly the *f*-electrons in the rare-earth and the uranium group. The absorption spectra of the rare-earth ions in crystals show definite structure even at room temperature when the temperature motion of the crystal lattice produces relatively large random disturbances. At very low temperatures, when the lattice vibrations are frozen out, the lines may become as sharp as the lines of free atoms. The interaction with neighboring atoms has not disappeared but has become very regular because of the regular arrangement of the crystal lattice. The lines of the rare-earth ion, therefore, have been shifted in the strong lattice field but have remained sharp. A review of such crystal spectra has been given by Joos (306).

Similar sharp line spectra at low temperatures have been observed for uranium compounds, particularly for the uranyl salts. Here the spectra are particularly rich in lines. As many as 1,000 individual absorption lines have been observed in the spectrum of a single compound. Also there is a well-developed fluorescence spectrum. It has been known for some time that the UO_2 ion is responsible for this spectrum, but a detailed interpretation of the observed structure presented difficulties. Work done on the Manhattan Project during the war and reported by Dieke & Duncan (297) made a beginning with a rational explanation of some of the observed phenomena. The main lines are given by a superposition of one of several electronic transitions and the molecular vibrations of the UO_2 ion. Vibrations of other parts of the molecules are often coupled with this (for instance, NO_3 vibrations have been identified in the nitrates). The spectra of all uranyl compounds are similar but differ greatly in details. The negative ion has a considerable influence and the symmetry of the crystal structure is very important. In the absorption spectrum, resonances between different frequencies may complicate the situation.

Isotopic substitutions (U^{238}—U^{235}, N^{14}—N^{15}, O^{16}—O^{18}, H—D) were very useful for the identification of the type of vibration. Another useful circum-

stance is that there are so many different uranyl compounds which can be compared. Similar spectra must be expected for the equivalent neptunium and plutonium compounds, but the available information is still very meager (312, 313)

A great deal of work has also been done on the spectra of phosphors where the situation is more difficult. The light emission resulting from phosphorescence is not a result directly of the properties of the molecules making up the crystal but a result of impurities that furnish so-called electron traps.

On the whole, the study of spectra of solids is still in the beginning stage. It may be expected that in the future much will be learned about the structure of matter in the solid state by the study of their spectra where favorable cases present themselves.

Spectrochemical Analysis

The application of spectroscopic methods to the determination of the chemical composition of alloys and other inorganic and organic substances has made tremendous strides during the past ten years. Quicker and more accurate and reliable methods have been devised. The instrumentation for the visible and ultraviolet as well as for the infrared has been improved so that these methods can now be handled in a routine fashion by unskilled personnel. The replacement of photographic methods by photoelectric techniques for the emission method has opened up new fields and has improved the results in many of the old fields.

Most of the methods of spectrochemical analysis have only very indirect, if any, connections with nuclear properties. The fast-growing bibliography is given in Scribner & Meggers' Index (327) to the literature on spectrochemical analysis. The subject begins to be well-covered by books dealing with the fundamental aspects as well as details of special analyses (317, 325, 329). Good spectra of most of the elements suitable for spectrochemical identification have been published by Gatterer & Junkes (322, 323).

For those concerned with the spectrochemical analysis of uranium and similar substances the carrier distillation method of Scribner & Mullin (328) is of particular importance. Ninety-eight parts of uranium oxide U_2O_3 are mixed with two parts of Ga_2O_3. There are other substances besides gallium oxide which may be used (325). In the spectrum of this mixture the uranium spectrum is suppressed whereas the lines of most impurities appear strongly, as uranium oxide is nonvolatile whereas the minute quantities of impurity vapors are swept into the arc by the carrier. Impurities with concentrations of less than a part per million can thus be detected. The copper spark method (321) has proved itself as a method for analyzing small quantities of material. The porous cup method (319) also has found many applications for the analysis of materials important for nuclear engineering.

Since the development of nuclear energy methods for the isotopic analysis of elements have become more than ever of great practical importance. The

mass spectrometer is the standard instrument for this. In some cases it may be replaced with advantage by spectroscopic methods. This may be done whenever there is an appreciable difference in the spectra of the two isotopes. In general, the spectroscopic methods will not have quite the accuracy of the mass spectrometer but may approach it in favorable cases. The use of a spectroscopic method may be more convenient and faster than the use of the mass spectrometer and thus recommend itself.

If use is made of atomic spectra, only the heaviest or the lightest elements are suitable as only with them are the isotopic shifts large enough. Figure 18 shows a direct photoelectric trace of a uranium line, which shows peaks for U^{238} and U^{235} which are the only isotopes occurring with fair abundance in natural uranium. This analysis can be made with any large or medium size spectrograph with relative ease, within a few minutes. If also U^{234} the third and least abundant isotope occurring in natural uranium is of importance, only the largest grating spectrographs or an interferometer can be used (see Fig. 14).

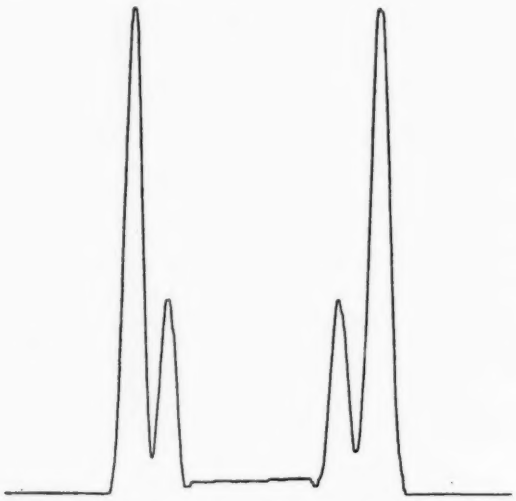

FIG. 18. Photoelectric trace of the 4244 uranium line taken with a medium sized grating spectrograph. The more intense line is a result of U^{235}, the weaker one a result of U^{238} (Argonne National Laboratory).

An isotopic analysis of He^3 and He^4 can be made spectroscopically without difficulty as the isotopic separations are quite large (see Fig. 10). They are even larger for the hydrogen isotopes (see Fig. 1). As hydrogen occurs in molecular form, attention must be given to possible preferential excitation of one of the isotopes or any other effect that might discriminate between them. This is equally important if the mass spectrometer is used. Such effects, however, are probably negligible for the heavier elements.

Usually, in order to separate the lines of different isotopes, large spectrographs are necessary. Figure 19 shows how an isotopic analysis for the hydro-

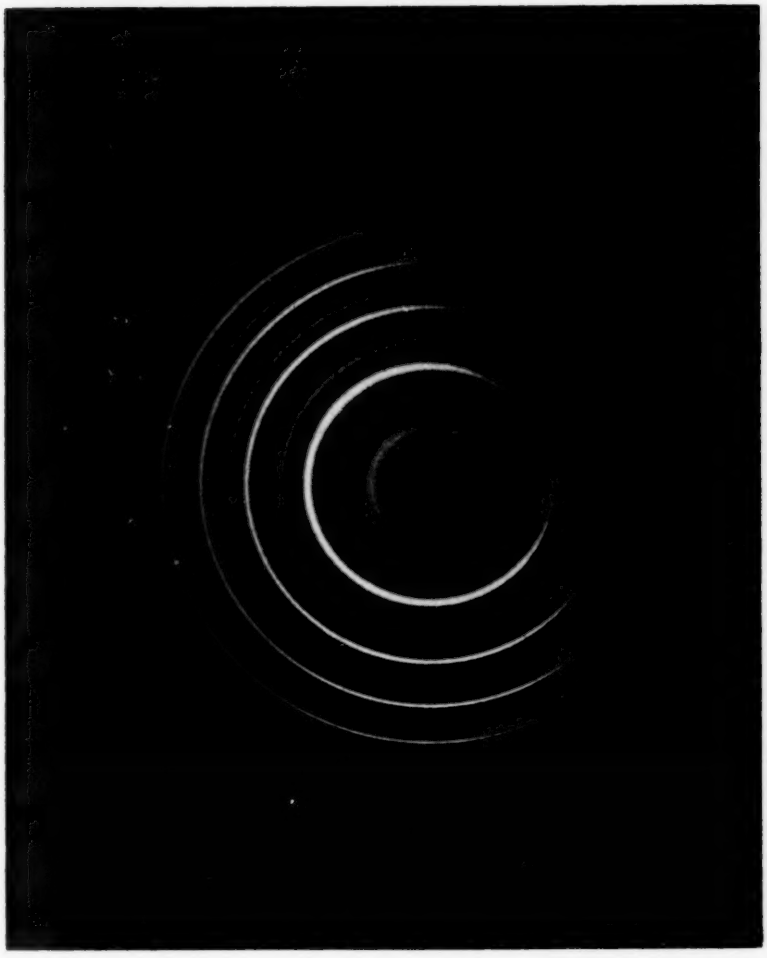

FIG. 19. Interferometer rings resulting from H_α (stronger) and T_α taken without a spectrograph (Johns Hopkins University).

gen isotopes can be made with very simple equipment without any spectroscope. A special small interferometer with small plate separation is used. It is just able to separate H_α, D_α, and T_α and, therefore, need not be of high quality. It was designed by Dr. Billings and made by Baird Associates. A red filter used with it will cut out any other radiation from a hydrogen discharge except H_α. A couple of lenses is all that is needed to project the interference rings. An ordinary photographic camera focused on infinity and a simple second lens are quite suitable. The relative intensities of the rings are at least a qualitative measure for the relative abundance of the isotopes. Whether this simple instrument will lend itself for accurate quantitative determinations remains to be seen.

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LOW TEMPERATURE PHENOMENA[1]

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Helium Isotope, Mass Four

The mass-four isotope of helium is believed to exist as a liquid, under its vapor pressure, from approximately 5.2°K. down to absolute zero. In the range from 2.19°K. to 5.2°K. the liquid, apart from one abnormality (the viscosity decreases as the temperature decreases), is "normal" in its properties i.e., behaves essentially like any other familiar liquid.

In the range 0°K. to 2.19°K. (the "λ-point") its behavior is, in most particulars, most unusual and quite unlike any other known fluid. For this reason, the first range has been called "helium I" and the second "helium II." Among these differences the following may be listed:

(*A*) At the λ-point a phase transition of the second kind occurs with a peak in the specific heat but no measurable latent heat.

(*B*) Below the λ-point the viscosity depends on the way it is measured. By Poiseuille flow it is of the order of 10^{-9} poise and by oscillating disc of the order of 3×10^{-5} poise. By comparison the viscosity of water at room temperature is 10^{-2} poise. Accordingly the name "superfluid" has been coined.

(*C*) The thermal conductivity, as determined by ordinary methods, is of the order of 300 cal./°C. cm. sec. at about 2°K. For comparison, pure Cu at room temperature is of the order of 1 cal./°C. cm. sec. As ordinarily defined the thermal conductivity is the ratio of heat flux, Φ (cal./sec. cm.^{2}) to temperature gradient (grad T) and is a constant. For helium II Φ is a nonlinear function of grad T with the temperature as a parameter. Hence the concept "thermal conductivity" has no clear meaning for helium II.

(*D*) As a first corollary to (*C*), Daunt & Mendelssohn found that helium II entering an insulated vessel through a narrow slit produces a cooling effect in the vessel and, conversely, upon leaving a heating effect is produced. This heating or cooling effect is found equal to ρST per unit volume transported where S is the entropy (per unit mass), ρ the density, and T the ambient temperature.

(*E*) As a second corollary to (*C*), temperature differences are propagated through the liquid not, as in the familiar case, by diffusion, but by an undamped dispersionless wave motion. The equation of temperature propagation is accordingly,

$$\nabla^2 T = \frac{1}{u_2^2}\frac{\partial^2 T}{\partial t^2}.$$

[1] This review is essentially a survey of papers published in 1950.

The velocity u_2 is temperature-dependent and of the order of 20 m. per sec. at 1.7°K. and zero at the λ-point, the former value being some 10 times smaller than the velocity of sound in the liquid. This phenomenon is generally called "second sound," a bad misnomer. No such effect exists above the λ-point or in any other known liquid.

(*F*) By applying heat, under suitable conditions, to a point in the liquid, it is possible to produce large ponderomotive forces ("Fountain effect"). In this connection a qualitative experiment of Kapitza is noteworthy. A small glass vessel, impervious to liquid helium, but with a very narrow neck, is totally immersed in a bath of helium II. The vessel lies on its side in the bath, with the neck horizontal, and is filled, via the neck, with liquid helium II. Just outside the neck is a small "paddle wheel" (similar to that in a Crooke's radiometer) free to rotate about a horizontal axis perpendicular to that of the bottle. When heat is supplied to the interior of the bottle (by radiation from outside) the paddle wheel rotates as though liquid were being continually ejected from the neck of the bottle. Nevertheless no loss of liquid from the bottle can be detected! No such effect, of course, exists above the λ-point, or in any other liquid.

(*G*) When an impermeable test tube is immersed vertically in a bath of helium II with its open end above the free surface it is found that the test tube will fill with liquid until the levels inside and out become equal. Conversely, if a test tube containing helium II is held above the bath the contained liquid will drip from the closed end back into the bath. The liquid flow has been shown to be via a thin mobile film (thickness $\sim 10^{-6}$ cm.) covering the surfaces, inside and out, of the beaker. The flow is from the higher to the lower gravitational potential and the rate depends on the temperature and on the least periphery of the connecting surface above the higher level, but not (within wide limits) on the gravitational potential difference.

(*H*) A hollow cylindrical vessel containing a number of concentric vanes and filled with helium II is found to have a moment of inertia which decreases as the temperature is lowered below the λ-point. The moment of inertia of the same vessel filled with helium I is substantially independent of temperature.

Most, if not all, of the above paradoxes can be explained, at least qualitatively, provided (following Tisza) we make the following simple, albeit surprising, assumptions as to the nature of helium II.

(*a*) If the density of the liquid be ρ one may think of this as composed of two parts, "superfluid" (density ρ_s) and "normal" (density ρ_n), such that $\rho = \rho_s + \rho_n$. Energetically the ρ_n group of atoms occupy a certain set of levels and the remainder (ρ_s) occupy a second distinct set. Transitions between the two sets are, of course, possible.

(*b*) The ratio $r = \rho_s/(\rho_n + \rho_s)$ is a monotonic function of temperature only, such that $r = 0$ at the λ-point and $r = 1$ at absolute zero.

(*c*) The viscosity of the ρ_s-liquid is vanishingly small. This is true of the entropy (S) also and this implies that the ρ_s atoms are energetically near absolute zero, i.e., are grouped in a ground state. ρ_n atoms will reside in higher or excited states, whence

$$\frac{\rho_n}{\rho} = \frac{S}{S_\lambda}$$

where S_λ is the entropy of the fluid at the λ-point.

(*d*) ρ_s atoms do not exchange momentum with either ρ_n or any other atoms.

For instance, the second-sound process may be very roughly pictured as follows. Thus $r=\rho_s/\rho=f(T)$ and if, at some point in the liquid, we suddenly increase the temperature ΔT the equilibrium here is disturbed, i.e., an excess of ρ_n atoms are created by raising available ρ_s atoms to this level from their ground state. Accordingly, ρ_s atoms from neighboring regions will flow toward the source of heat, leaving the places where they came from with a momentary excess of ρ_n atoms or effectively raising the temperature there. Thus ΔT will propagate throughout the liquid. Also the curious effect (F) is explained by this procedure and (*d*) above. The paddle wheel is run by ρ_n atoms balancing, by continuity, the inward ρ_s flow. The latter keeps the bottle full, the two streams commingling in the neck of the bottle without interaction.

Two questions now naturally arise—namely, whether the above assumptions can be made intelligible by consideration of the dictates of either classical hydrodynamics or quantum mechanics. The answer to the first of these is clearly "No," and, to the second, "Perhaps." London was the first to point out that an ideal gas of mass particles obeying Bose-Einstein statistics showed properties closely analogous to some of the requirements listed above. In particular it is a property of this statistic that below a certain temperature (T_c) a certain fraction of the atoms are "condensed" in a ground state of high degeneracy [compare (*b*) above]. If we identify these atoms with ρ_s then, for an ideal gas of atoms of mass four,

$$\rho_s = \rho\left\{1 - \left(\frac{T}{T_c}\right)^\sigma\right\}$$

where

$$\rho = \rho_s + \rho_n$$

and

$$T_c = 3.14°\text{K}.$$
$$\sigma = \tfrac{3}{2}.$$

Also, at T_c, a discontinuity in the specific heat occurs in this model, although it is of a different form from the actual discontinuity found. We have then, on orthodox quantum mechanics, a hint, but no more than that. An ideal gas is far from a liquid,—interactions occur. If we attempt to "fit" the gas theory to the experimental liquid good results are obtained (in the range

from the λ-point to ~1°K.) for $\sigma \cong 5.6$, which is in the right direction since interactions will tend to increase σ.

Tisza developed these ideas into a phenomenological theory which, among other things, predicted the existence of the second sound some six years prior to its experimental discovery by the Russian physicist Peshkov. Somewhat later than all this Landau independently developed a theory of helium II

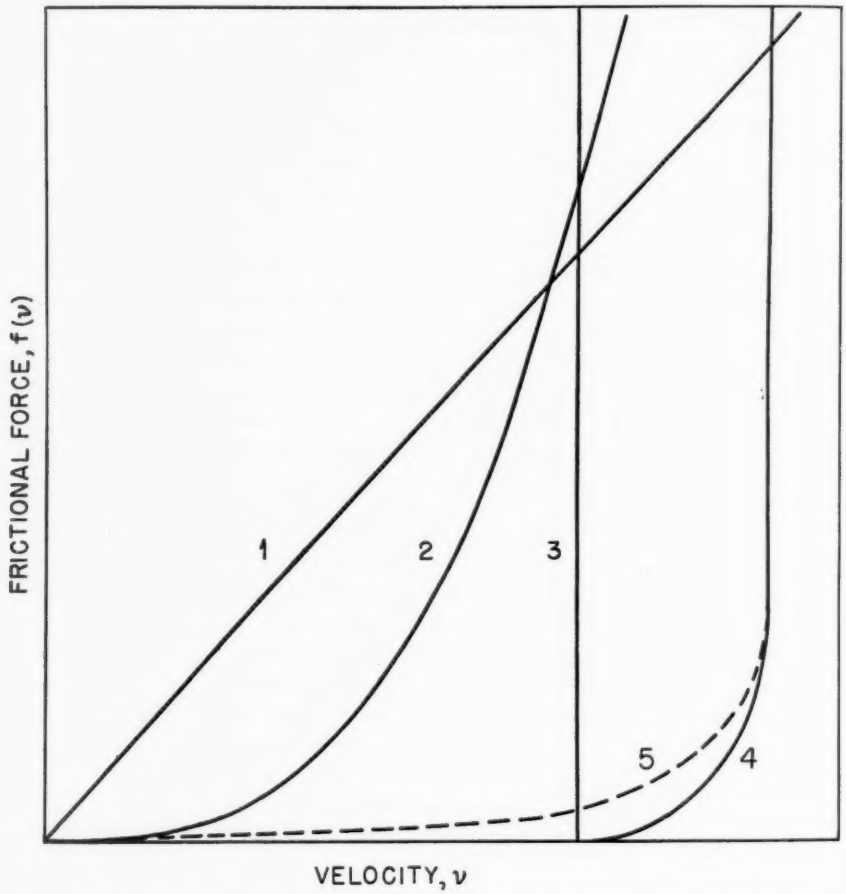

FIG. 1. Dependence of the assumed frictional force in the superfluid on velocity (after Atkins).

1) Ordinary viscous flow.
2) Gorter-Mellink flow $f(v) \sim (v_s - v_n)^3$.
3) Daunt-Mendelssohn critical velocity v_c.
4) Combination of frictionless flow up to v_c plus a part which can raise the velocity above v_c but is dependent on frictional retardation.
5) Flow never completely frictionless.

which, while very similar in its results, is, at least on the surface, very different in its approach. Here an ambitious attempt is made to formulate a quantum hydrodynamics on the basis of certain quantum commutation rules. The approach has been criticized by London, Tisza, and others and it has been felt that the Landau formulation contains "hidden" assumptions not more easily justifiable by orthodox quantum mechanical principles than are the basic assumptions, listed above, inherent in the other theory. Nevertheless, in some particulars, Landau's theory is in much better agreement with experiment than that of Tisza-London.

We may now consider assumption (*d*) above in the light of recent experimental work, and, in particular, in connection with two kinds of experiments, namely, "film" flow as mentioned under (*G*) above, and flow through narrow slits under small external pressure heads. In order to account for the observed properties of film flow Daunt & Mendelssohn had to suppose that the ρ_s flow was truly frictionless only up to a certain "critical" velocity (v_c). Such an idea is necessary to account for the observed independence of the bulk flow through the film on the gravitational potential difference.

On the other hand Gorter & Mellink, on the basis of observed flow through narrow slits, postulate a frictional force between ρ_s and ρ_n approximately varying as the cube of their relative velocity. Figure 1, taken from a recent paper by Atkins (1), shows schematically the various possibilities. Atkin's most recent work on film flow seems best explained by Curve 4, although Curve 5 is not entirely excluded.

In the original experiments on film flow (Daunt & Mendelssohn, 1939) it was thought that the film transport was independent of the nature of the surface over which the film flowed. Recent experiments, however, have indicated that this is probably untrue. Thus Mendelssohn & White (2) have investigated the liquid transfer rate via the film over surfaces of glass, platinum, and nickel, using a modification of the "test tube" technique. Elaborate precautions were taken to prevent gas impurities (e.g., air) from coating (by solidification at the low temperatures) the test surfaces, since it had been shown previously by Mendelssohn & Bowers that such impurity

TABLE I

TRANSFER RATES (IN CM.^{3}/CM. SEC.$\times 10^5$) OVER VARIOUS SURFACES

Temp. (°K.)	Pt Cleaned	Pt Cleaned and baked	Pt Cleaned and polished	Ni Cleaned and baked	Glass Cleaned
1.2	15.9	21.4	22.4	24.3	7.3
1.5	16.9	20.8	21.0	22.7	7.1
1.8	13.0	16.5	17.0	17.0	6.2
2.0	6.9	9.8	9.9	9.5	3.8

coatings led to anomalously high transfer rates presumably by increasing the periphery of the surface. These results are shown in the accompanying table.

More recently Boorse & Dash (3) have carried out a similar investigation using, however, a non-optical method of observing the flow rate and the results, taken from their paper, are given in Table II.

TABLE II

FILM TRANSFER RATES OVER DIFFERENT SURFACES

	1.3°K.	1.5°K.	1.8°K.	2.0°K.
Pyrex glass	7.6	7.5	—	—
Lucite	14.4	16.6	11.5	—
Stainless Steel	10.4	9.7	6.8	3.3
Lead	33.3	31.1	26.6	16.5
Cold-Rolled Steel	10.5	—	—	—
Machined Copper	14.8	14.8	12.4	7.9
Polished Copper	23.0	19.8	14.7	7.1
Etched Copper	51.2	49.0	40.0	24.8
Etched Copper Oxidized	26.0	24.8	20.4	13.7

The above experiments do not, of course, enable us to determine the value of the film velocity. For this, it would be necessary, in addition to the transfer rate (in $cm.^3$ per second per centimeter of periphery) to know the film thickness. A simultaneous measurement of these two quantities has recently been made by Jackson & Henshaw (4) employing a very elegant method. The test tube in this case is of stainless steel with a 4 mm. inside diameter and a glass capillary side arm to render visible the liquid level in the vessel and hence observe the transfer rate. The outside of the steel vessel has a polished 2 mm. wide "flat," and the thickness of the film (in transit) is determined by an optical method which depends on the fact that when plane polarized light is reflected from a polished metal surface it becomes elliptically polarized. The ellipticity and orientation of the ellipse depend on the optical constants of the metal, the angle of incidence, and the wavelength. These constants are changed by the superposition of a film of transparent material (i.e., the helium film) and the measured changes give thickness of the film if its refractive index is known. Calibration is accomplished by using a barium stearate coating of a known few molecules thick, the thickness of this coating varying from top to bottom of the mirror in a known way. The experimental arrangement is shown, schematically, in Figure 2. The results, together with the derived film velocity, are given in Table III. Since theory indicates (see below) that the film thickness d, should depend on the height above the liquid level H, these measurements were made at $H=1$ cm. Of course, the refractive index assumed for the film is that of the bulk liquid

which is probably reasonably safe. These measured velocities must be regarded as "critical" velocities for the superfluid component of the film at the several temperatures. The composition of the film will presumably be the same as that of the bulk liquid at the temperature in question and only the superfluid fraction will be mobile. Above this critical velocity the superfluid atoms begin to lose the property ascribed to them under assumption (*d*) above. Perhaps some sort of "turbulent" motion sets in. The fact that a film forms on the solid surface at all is, of course, because of the fact that adsorbed forces greatly outweigh the Van der Waals' forces which are known

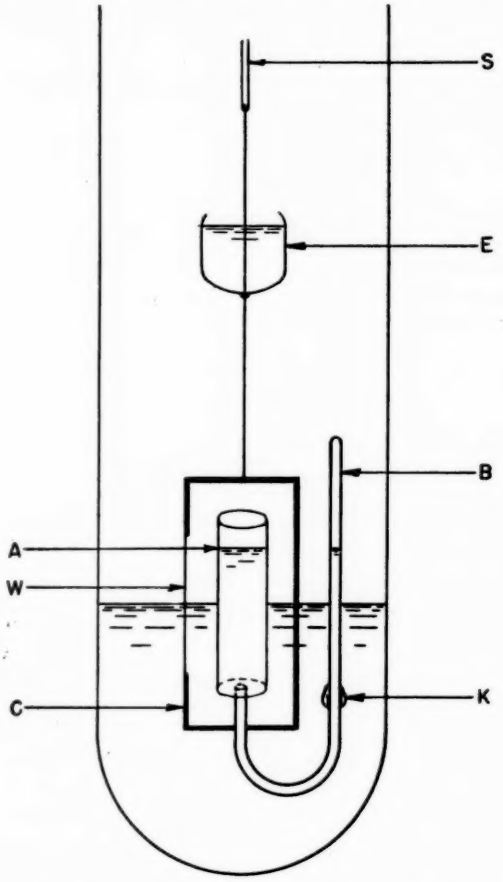

FIG. 2. Schematic of apparatus used to measure, simultaneously, film transport and film thickness [after Jackson & Henshaw (4)].

A—stainless steel beaker
B—glass tube
C—copper radiation shield
W—window
E—liquid helium heat shield
S—suspension.

TABLE III

TRANSFER RATE, THICKNESS AND VELOCITY OF THE HELIUM FILM

T (°K.)	cm.³/sec. cm.	Thickness (cm.)	Velocity (cm./sec.)
1.1	16.9×10^{-5}	1.63×10^{-6}	72
1.3	16.9	1.63	72
1.5	16.8	1.66	68
1.7	16.1	1.82	60
1.9	12.8	1.94	29

to be weak in helium; in this respect the film differs only in size from that produced by surface tension in ordinary liquids.

By comparison with the above, the film thickness has also been measured recently using an indirect method by Atkins (5). Since the film possesses momentum, the level of the liquid inside the test tube will oscillate about its equilibrium position and, by applying suitable assumptions, the film thickness may be deduced from measurements on this. In particular the variation of film thickness with the height of the film above the liquid level may be deduced. Atkins finds that the thickness, d, varies with the height, H, according to

$$d = \frac{k}{H^n}$$

where

$$k \sim 2 \times 10^{-6}$$

$$n \sim 0.14 \ (H \text{ between 0.5 cm. and 5.0 cm.})$$

The problem of the variation of d with H had previously been treated theoretically by two distinct approaches. Thus Schiff (36) and Frenkel (37) assume the film is produced by adsorptive forces between the wall and helium atoms; for this $n=\frac{1}{3}$. Bijl, de Boer & Michels (38) suppose the mechanism to be related to the zero-point energy of the helium atoms (which is large) confined within the film thickness (which is small). This gives $n=\frac{1}{2}$. It appears therefore that neither theory is in satisfactory accord with the above experiment. Nevertheless, lacking direct measurements on d (of the Jackson-Henshaw type) as a function of H, it would be premature to reject either theory since Atkin's measurements involve a series of assumptions, the truth of some of which are not obvious, although, it is true, that his results are in fair accord with those of Jackson & Henshaw for $H=1$ cm.

During the year under review further important experimental work on the second sound has been reported. The original velocity versus temperature measurements of Peshkov [1946] were taken down to 1.1°K., but it was realized that values at still lower temperatures would be of great interest for the following reason. Down to the vicinity of 1°K. the theories of Tisza and

Landau predict about the same course for this velocity; thereafter the divergence becomes ever larger until, at the absolute zero, Tisza believes that $u_2=0$ whereas Landau thinks that $u_2=u_1/\sqrt{3}$, wherein u_2 is the second-sound velocity and u_1 that for normal sound in helium II.

Herlin & Maurer (6) first extended the measurements to about 0.8°K., but this is not sufficiently low a temperature to permit a clear-cut decision. Then Pellam & Scott (7) performed a semiqualitative experiment using the

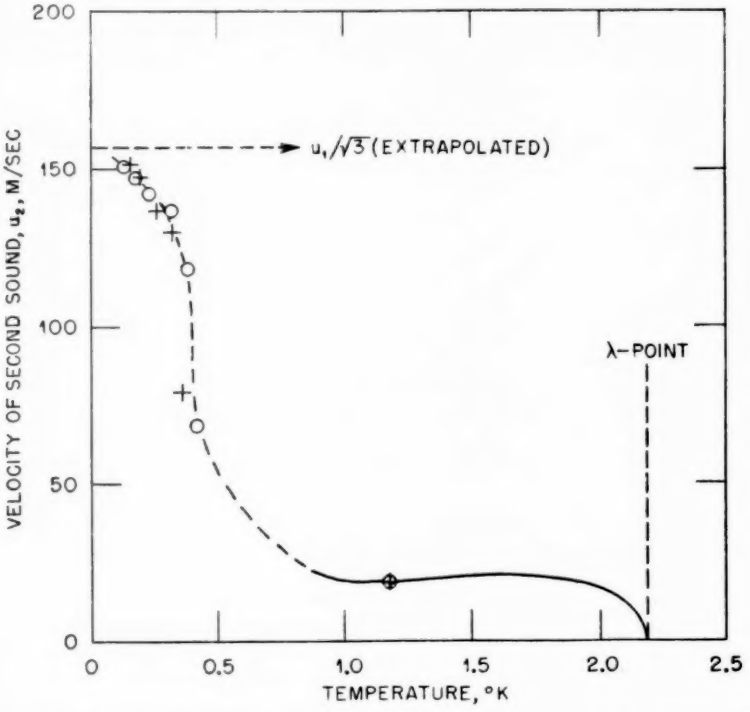

FIG. 3. Second-sound velocity as a function of temperature [after Atkins & Osborne (8)].

Full line—previous observations.

Dotted line—present experiment.

difficult technique of adiabatic demagnetization which, for the first time, showed that the second-sound velocity behaved more nearly in the way which Landau had visualized. Now Atkins & Osborne (8), using a method very similar to that of Pellam & Scott, have extended the measurements to the vicinity of 0.1°K. These results are shown in Figure 3. Although the velocity, u_1, has not been measured below 1.5°K. and, in consequence, a somewhat uncertain extrapolation is necessary, it nevertheless now appears certain that Landau's theory is to be preferred in this particular case.

It has previously been mentioned that the theories of Tisza and Landau are, on the surface, vastly different in their approach. Nevertheless, there are close analogies between the two. Thus both are "two fluid" theories and one of their main differences appears to lie in how the normal component of the liquid is to be constructed. Both consider the superfluid component to be a sort of "condensed" phase and, in neither does the reason why such a phase should be frictionless emerge clearly. In both theories, therefore, the main attention is focussed on the normal or nonfrictionless ("excited") phase.

In particular Landau believes that it follows unambiguously from quantum mechanics that for every slightly excited macroscopic system a con-

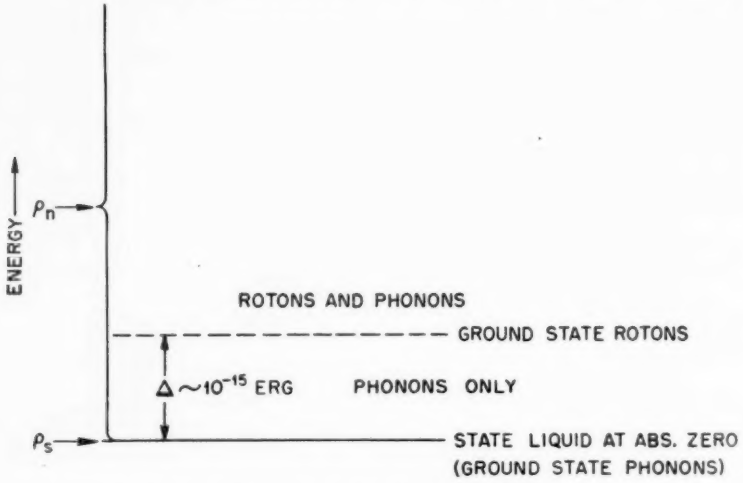

FIG. 4. Schematic of the phonon-roton spectra.

ception of "elementary excitations" may be introduced. These, for a liquid can be: (*a*) "phonons"—quantized sound waves of the Debye type; or (*b*) "rotons"—quantized vortex motions. At sufficiently low temperatures both types of excitations can be thought of as constituting an ideal gas. Figure 4 shows, schematically, the energy spectrum for these excitations assumed by Landau. Both types of excitation form a continuous spectrum but the *ad hoc* assumption is made that the roton spectrum is separated by an energy gap, Δ, from the phonon spectrum. According to Landau, then, ρ_n is the aggregate of the excited phonons and rotons; ρ_s is that part of the liquid helium "left behind."[2]

[2] The assumed gap Δ between the roton and phonon ground states is evaluated by computing the specific heat of the sum of the two excitations and comparing it with the empirical data in the range 1–2°K. This gives $(\Delta/k) \backsim 8$–9°K. and also the roton mass $\backsim 7$–8 helium atom masses. At 1°K. there are 2×10^{18} phonons (per cm.^{3} liquid helium) and 7×10^{18} rotons, whereas at 0.2°K. this is reduced to 3×10^{15} phonons and $\backsim 10^3$ rotons, the rapid attenuation of rotons resulting from the gap Δ. At the lower temperature the mean phonon energy is 5×10^{-22} erg, i.e., well below the roton ground

Figure 5 shows the temperature dependence of respectively, the phonon and roton components of ρ_n. This figure is merely illustrative, since it is not possible to draw the ordinate to any kind of scale. Thus at 0.2°K., for instance, the ratio of (ρ_n/ρ) phonons to (ρ_n/ρ) rotons is $\sim 10^{11}$.

On the other hand Tisza's view is that phonons are associated with the liquid as a whole, i.e., do not form a part of the normal component of the fluid. It is this fact plus the existence of the gap Δ which leads to the differ-

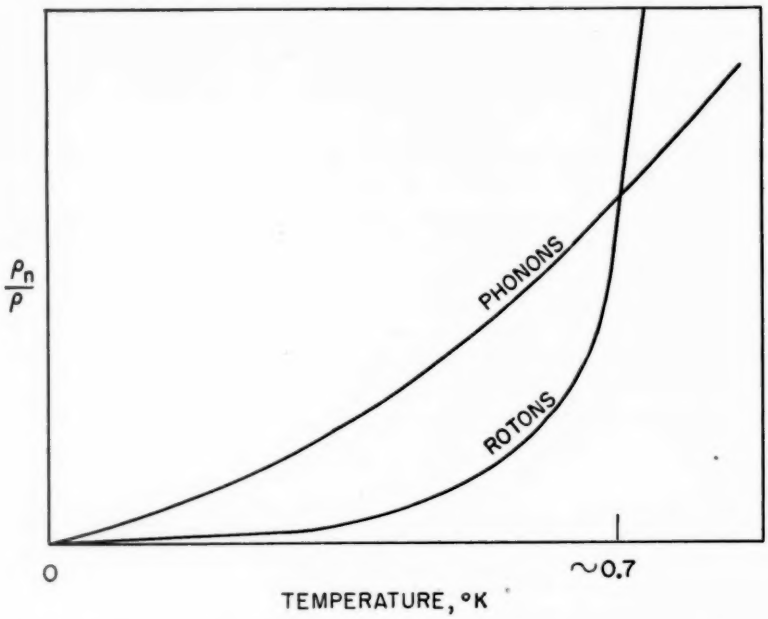

FIG. 5. The temperature dependence of, respectively, the contributions of the rotons and phonons to the normal part of the liquid (schematic only).

ence, noted above, between the predicted values of the second-sound velocity in the vicinity of absolute zero.

It should also be remarked that the Bose-Einstein statistic is not invoked in the Landau formation[3] whereas in the Tisza-London theory it is pretty nearly the crux of the whole matter.

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state. At temperatures well below 1°K., therefore, the normal component of the liquid is virtually entirely phonons and hence the specific heat of helium II, in this range, should obey a T^3 law, which it in fact seems to do. However, the computed Debye temperature for phonons is 29°K., which is nearly twice that observed for helium II by Bleaney & Simon in the range 0.25°K. to 0.8°K.

The value $u_2 \to (u_1/\sqrt{3})$, $T \to 0$ is, however, independent of the Debye temperature.

[3] It should be stated that the "phonon" gas obeys Bose statistics and this is probably true of the rotons also. However, this has no bearing on the statistics obeyed by the nuclei of the atoms which form the liquid.

It is possible, although it has not as yet been clearly demonstrated, that the Tisza-London theory could be "fixed up" on this point (e.g., the role of phonons) but until, and if, this is done it appears to be a rather serious defect in the light of the Atkins-Osborne experiment. For the most recent critique of the two theories, by the authors themselves, see references (9) and (10).

An experiment which at first sight ought to throw a good deal of light on the helium II problem has recently been reported by Osborne (11). Here helium II is placed in a bucket rotating about a vertical axis and observations are made on the shape of the free liquid surface. In an ordinary liquid this should be parabolic, i.e.,

$$z = \frac{\omega^2}{2g} r^2$$

where z and r are the vertical and radial co-ordinates, respectively, of a point on the surface, ω the angular velocity, and g the acceleration due to gravity. This expression does not involve the density (ρ) since both the centripetal and gravitational forces on an element of the fluid are proportional to its density.

For helium II, however, the situation is supposedly different. Here $\rho = \rho_n + \rho_s$, and ρ_s may not be accelerated into rotation, although it will, of course, possess mass and be subject to gravitational attraction. For this case the above expression is modified to

$$z = \frac{\rho_n}{\rho} \frac{\omega^2}{2g} r^2$$

and in addition, as Osborne shows,

$$T(r) = \frac{1}{2} \frac{\omega^2 r^2}{S_\lambda} + T(0)$$

where $T(r)$ is the temperature of the surface at distance r from the axis and S_λ the entropy of helium at the λ-point. This temperature gradient will give rise to a fountain effect pressure which replaces the centripetal force present in an ordinary liquid.

The results of several runs (together with a schematic of the apparatus) are given in Figure 6. The full line is a plot of the equation for an ordinary liquid. Within the experimental error it is clear that no such effect as predicted for a superfluid occurs.

Osborne's view that the negative result is connected with critical velocity considerations may, of course, be correct but there are other possibilities. Onsager believes, as a result of some unpublished computations, that the effect on the meniscus is indeed present but is in the nature of a "fine structure" which would be well below the limit of observation possible in Osborne's experiment. He finds that it is not possible to construct a wave function for the liquid rotating as a whole; rather one must suppose that the circulation is quantized in units of the order of $h/m \cong 10^{-3}$ cm.^{2}/sec.

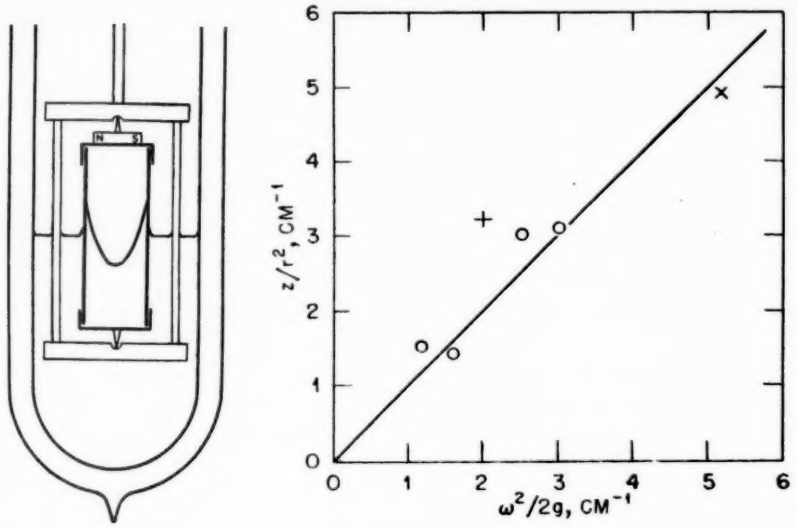

FIG. 6. Schematic of the apparatus and results in the rotating fluid experiment [after Osborne (11)]. In the curve on the right the full line is a plot of $z/r^2=\omega^2/2g$, and the experimental points are as follows:

O	1.20°K.	$\rho_n/\rho=0.03$
+	1.40°K.	$\rho_n/\rho=0.08$
×	1.59°K.	$\rho_n/\rho=0.18$.

(h=Planck's constant; m=the mass of the helium atom); and with this consideration the above-mentioned "fine structure" occurs.

HELIUM ISOTOPE MASS THREE

The helium isotope of mass three, even before it was concentrated in sufficient quantity to make measurements possible, was the object of a great deal of interest among cryogenic specialists. Helium four is a spinless particle; on the other hand, helium three, possessing an odd number of nucleons, should possess spin. If, then, the superfluid properties of liquid helium four depend on Bose-Einstein statistics as the Tisza-London theory supposes, liquid helium three should not be superfluid since its particles ought to obey Fermi statistics. It was in fact not even sure that He^3 could be liquefied at all.

The subsequent experiments of Sydoriak, Hammel & Grilly (39) on one hand and Weinstock, Osborne & Abraham (40) on the other have gone some distance in answering both questions. The first-named authors have shown that pure He^3 does liquefy with a critical temperature of 3.34°K. and a normal boiling point at 3.2°K., and, further, remains liquid under its vapor pressure down to at least 0.76°K. The latter experimenters, using the

Poiseuille viscosity as the criterion for superfluidity, have shown that pure He^3 is not a superfluid at any temperature down to about 1°K. In addition they find that the viscosity increases from 22μ poise at 2.79°K. to 30.4μ poise at 1.04°K., an effect exactly opposite to the behavior of either helium I or helium II.

Most cryogenic laboratories, in fact all outside the A.E.C. group, have not had pure He^3 available and have had to content themselves with quan-

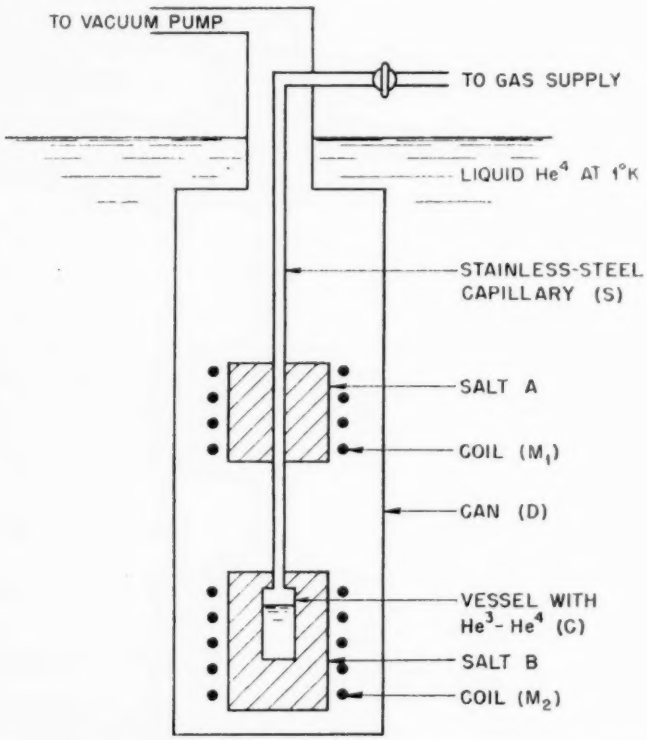

FIG. 7. Schematic of the experimental arrangement used to determine the λ-points in He^3-He^4 mixtures [after Daunt & Heer (12)].

tities of the order of 3 cubic cm. (S.T.P.) of about 88 per cent He^3, the balance being He^4. Nevertheless important work, even with such minute quantities, has been accomplished.

Recently Daunt & Heer (12) have looked for superfluidity in such a mixture down to 0.38°K., and the basis of their method is as follows. Imagine a test tube closed at both ends and containing liquid helium II condensed in the bottom. Let this test tube be partially immersed in a Dewar also containing liquid helium II, such that the two liquids are in thermal contact. Suppose also the top of the closed test tube is at a higher temperature (room

temperature, say) than the bath. A helium II film will form on the walls of the test tube in the usual way and, under the influence of the temperature gradient, the superfluid part will flow, through the film, up the walls of the tube to the higher temperature. The film will, of course, cease to exist at a place on the tube wall where the temperature equals that of the λ-point. Here the film will evaporate, and, since the top of the tube is closed, the resulting vapor will flow back down the tube and recondense at the liquid surface, the heat of condensation being carried away to the outer bath. In other words the presence of the film will show up as an added "heat leak" into the liquid, and if the latter had no contact with a heat sink (the outer bath) it would gradually increase in temperature even if it were otherwise adiabatically isolated.

If, for the moment, it is assumed that pure He^3 has a λ-point (below 1°K.), then mixtures of He^3-He^4 should have a series of λ-points depending on the relative concentrations. Hence the presence of a λ-point in He^3 could be detected even in an He^3-He^4 solution by investigating various concentrations at various temperatures, using the added heat leak resulting from the mobile film as a criterion. This is substantially what the above authors do.

Since the measurements extended to about 0.4°K., adiabatic demagnetization of a salt was employed. Figure 7 shows a schematic diagram of the arrangement. The mixture under investigation is condensed in the small vessel C via the capillary S, the heat of condensation being carried away via a small amount of helium gas in the can D which is then pumped to high vacuum and salts A and B demagnetized such that the temperature of A is somewhat higher than that of B. The magnetic susceptibility of A and B were determined by measuring the inductance of coils M_1 and M_2. Hence the Curie temperature[4] could be found. Observations (by ballistic galvanometer) were now made on the temperature of B as a function of time. A typical result is shown in Figure 8. For a 79 per cent He^3 concentration, the heat leak (proportional to the slope of the curve) is suddenly reduced commencing at the point "a" which corresponds to a temperature of 0.65°K. On the above reasoning this, then, is the λ-point for the above concentration. The highest concentration of He^3-He^4 available to Daunt & Heer was about 89 per cent He^3, and, with this mixture, the λ-point was found to be 0.38°K. This means that just above 0.38°K. (with 89 per cent He^3) no film flow takes place, i.e., this mixture is not superfluid. Hence if pure He^3 has a λ-point at all it must lie below this temperature.

This is brought out rather more clearly by Figure 9 wherein the λ-points relative to pure He^4 are plotted as a function of concentration. The measurements in the lower concentration range are a result of Abraham, Weinstock

[4] The "Curie temperature" is the temperature deduced from the measured magnetic susceptibility (χ) by assuming the latter obeys Curie's Law, $\chi = \text{Constant}/T$. The temperature so deduced differs only slightly from the Kelvin absolute temperature in the range covered by these experiments.

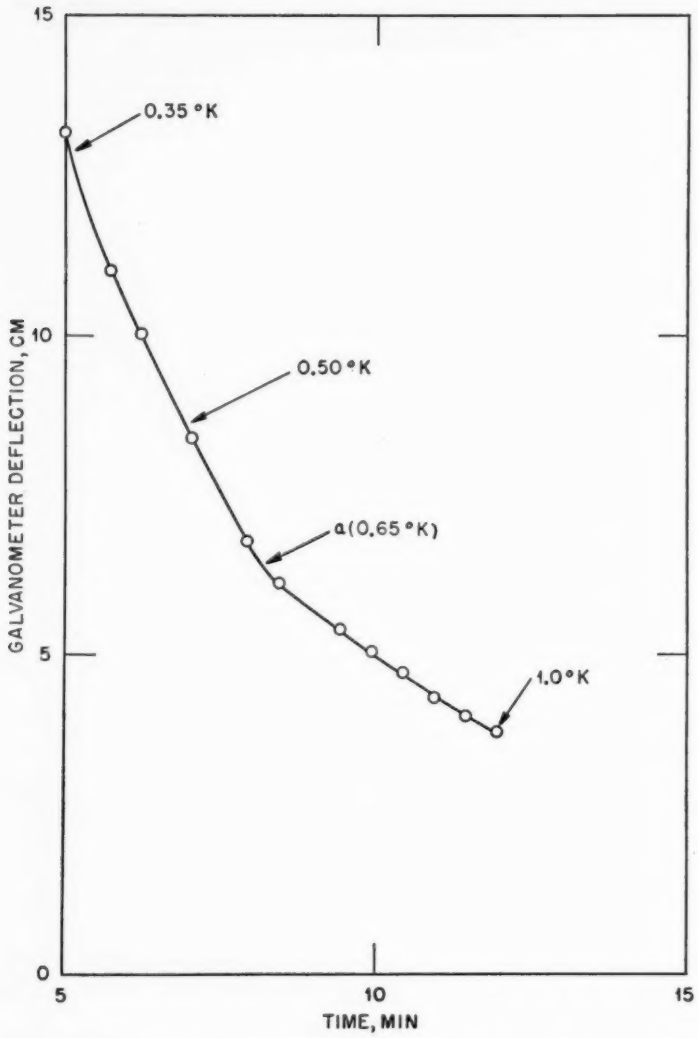

FIG. 8. Typical warm-up curve of Salt B (FIG. 7) for a 79 per cent He^3 solution. The point "a" marks the λ-point [after Daunt & Heer (12)].

& Osborne (13) using the same method for the mixtures as employed by them in their original investigations on pure He^3.

It appears therefore reasonably certain that pure He^3 does not exhibit superfluidity above 0.38°K. It would be of the greatest interest to extend measurements on pure He^3 to the lowest possible temperature (~0.01°K., for instance) for the following reason: there appears to be no way of dis-

tinguishing between He^3 and He^4 in Landau's theory—in other words this theory would predict superfluidity in pure He^3 without, however, fixing its λ-point; on the other hand, the formulation of Tisza-London prohibits superfluidity in He^3 because of the statistics (Fermi) obeyed by this particle.

Apart from the above, a considerable interest attaches to the thermodynamics of the solutions themselves, in particular the question as to whether the λ-point transitions are of the first- or second-order. In pure He^4 the λ-transition is, as has been mentioned, second-order. This question, for the solutions, has been considered, theoretically, by Stout (14), de Boer (15), de Boer & Gorter (16), and Rice (17). Apart from the assumptions as to

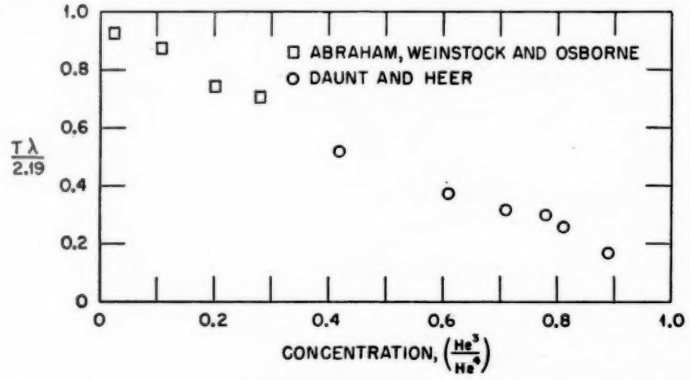

FIG. 9. The "reduced" λ-point as a function of He^3 concentration.

first- or second-order transition these theories are also based on the suppositions that (*a*) pure He^3 is not superfluid, and (*b*) that, in solution, the He^3 atoms dissolve in the ρ_n-fraction of helium II only. The evidence for (*a*) has been discussed above; that for (*b*) also exists from the experiments of Taconis, Beenakker, Nier & Aldrich (18). With the above and with, in addition, some necessary, though admittedly *ad hoc*, assumptions as to the free energy of helium II it is possible to compute the variation of the λ-temperatures as a function of He^3 concentration. The experimental results given in Figure 9 are in fair agreement with either a first- or second-order transition—it is impossible to decide which.

Evidence, however, of a different kind points to the transition as being second-order, the experiment having been performed by Weinstock, Osborne & Abraham (19). With a first-order transition de Boer shows that the solution should split into two liquid phases (when below its λ-point) in equilibrium with each other and with the vapor. It follows then, from the Phase Rule, that when two liquid phases and a vapor phase, in a two component system, are in equilibrium there can be only one degree of freedom, i.e., the vapor pressure must be a function of temperature alone and thus independent of relative concentration.

Accordingly, the above authors have investigated the vapor pressure of 20.3 per cent He^3 and 25.5 per cent He^3 as a function of temperature below either λ-point. Their results are shown in Figure 10. Clearly the assumption of first-order transition is not borne out, at least down to their lowest temperature (~1°K.) and up to their highest concentration (~25 per cent He^3).

The above work has established that solutions of He^3-He^4, up to at least 89 per cent He^3, still show some of the phenomena of superfluidity, (e.g., λ-point, film phenomenon, etc.). It is therefore a matter of some interest to investigate other superfluid phenomena in these solutions, and, in

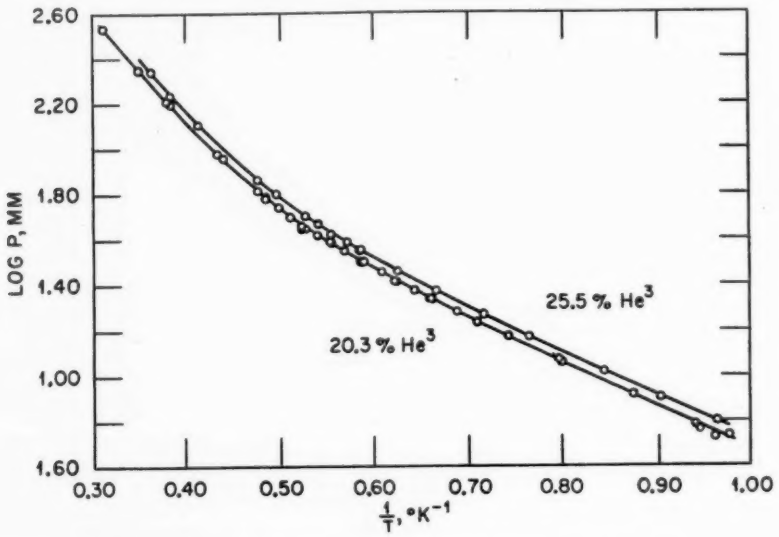

FIG. 10. The vapor pressures of two solutions of He^3 in He^4 [after Weinstock, Osborne & Abraham (19)].

this connection, measurements on the second sound have recently been carried out by Lynton & Fairbank (20). These authors have studied the variation of the second-sound velocity with temperature for several dilute solutions (up to ~1 per cent He^3). Prior to this Pomeranchuk (21) had predicted theoretically that there should indeed be a marked influence on the velocity due to even minute amounts (~0.1 per cent) of He^3 dissolved in He^4.

Two technical difficulties are involved in such experiments—one artificial and the other natural. The first involves the small amounts of He^3 available to the non-A.E.C. laboratories forcing the employment of "micro" equipment with all the troubles inherent in such. The second difficulty is more fundamental. In pure He^4 the mechanism of heat conduction is, as we have mentioned previously, by a process of "internal convection." Since the ratio ρ_s/ρ depends on temperature only, a temperature gradient in the liquid

should produce a diffusive flow of ρ_s to the high temperature end (where ρ_s atoms are being converted to ρ_n) and a balancing flow of ρ_n in reverse. It has been shown experimentally, some time ago, that when He^3 atoms are present they will partake in the normal but not in the superfluid flow of He^4 (22). Hence the net effect of a temperature gradient in the He^3-He^4 solution is to separate the He^3 atoms from the He^4 by driving the former in the direction of the heat flow. This has been called the "heat flush" effect. If, then, we are to measure second-sound velocities in the usual way by producing a temperature pulse at one point in the fluid and detecting it at a later time and at a known distance from the transmitter, it is clear that this "heat flush" effect can be very awkward in disturbing the spatial equilibrium between He^3 and He^4 in the solution under investigation.

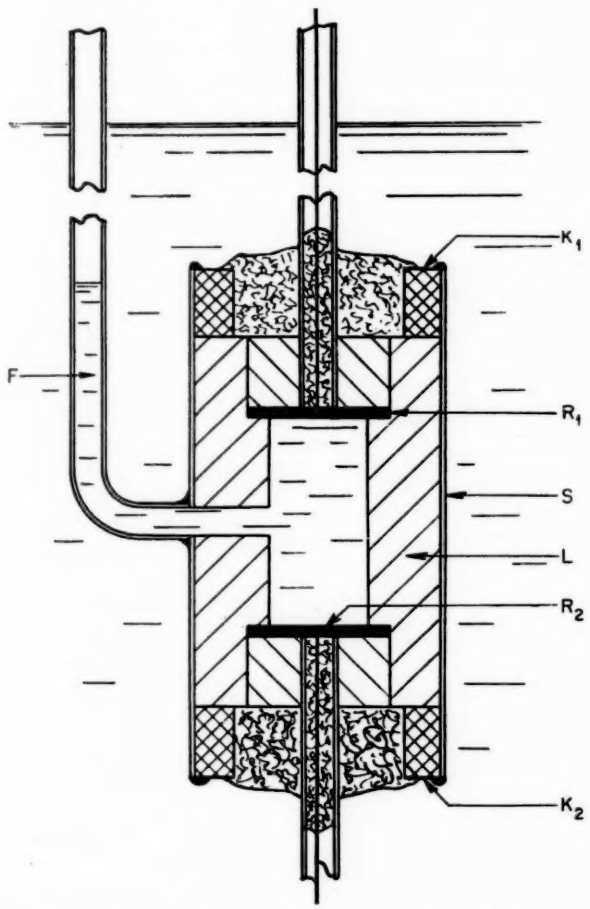

FIG. 11. Schematic of apparatus used to measure the velocity of second sound in He^3-He^4 solutions [after Lynton & Fairbank (20)].

Figure 11 shows the essentials of the apparatus used by Lynton & Fairbank, A small cavity (3 mm. diameter, 10 mm. long) is formed in a Lucite block (L) containing carbon strip resistors (R_1 and R_2) at each end. A metal sleeve (S) makes the whole assembly vacuum tight and the He^3-He^4 mixture may be condensed in the cavity via the metal capillary (F). The whole is immersed in a bath of ordinary liquid helium. R_1 acts as a transmitter of heat pulses and R_2, with a D.C. current through it, acts as a resistance thermometer receiver. The transit time of the heat pulse between R_1 and R_2

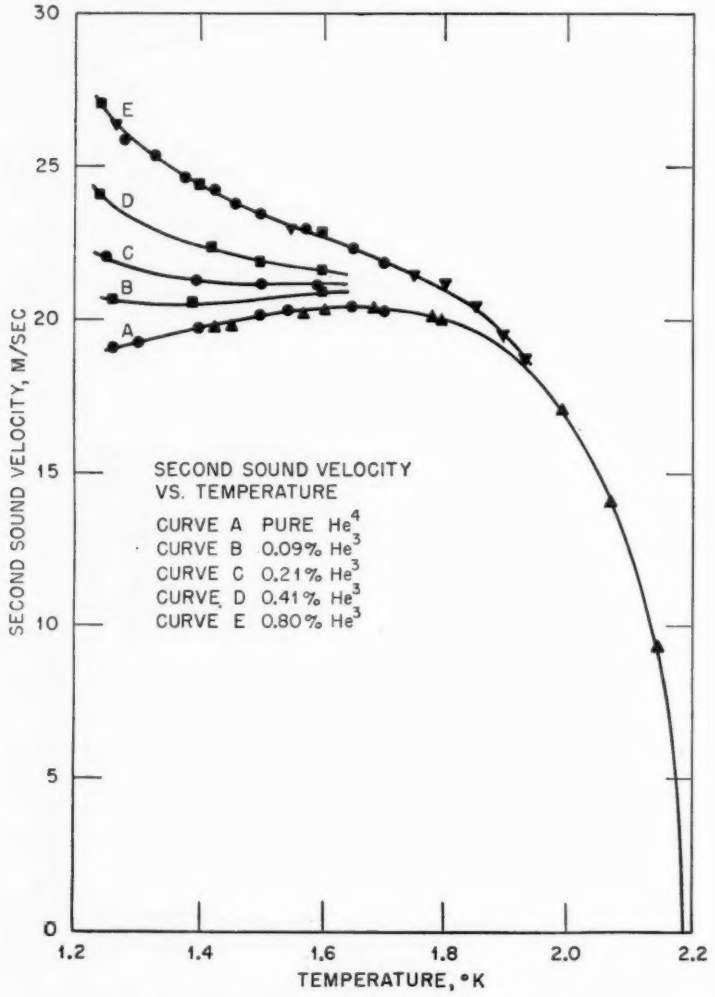

FIG. 12. Second-sound velocity as a function of temperature for several He^3 solutions [after Lynton & Fairbank (20)].

was measured by standard Radar techniques (23, 24). In order to minimize the effect of "heat flush" the transmitter was fed single pulses of heat and, simultaneously, the receiver had short pulses of D.C. current. In this way the heat fed into the solution was kept at a very low value. Figure 12 shows the results—the curve for pure He^4 being in excellent agreement with previously reported values. The results for He^3-He^4 are also in general agreement with the prediction of Pomeranchuk's theory.

The reason for the increase in second-sound velocity with He^3 concentration can perhaps be pictured roughly as follows. The He^3 is concentrated in the normal component of the liquid and, under the action of the heat pulse, moves with it relative to the superfluid component. This displaced He^3 must rediffuse and this is a comparatively slow process. The net effect of this is to endow the fluid with a larger "effective mass," i.e., make the process more like that which occurs with ordinary sound, the latter having, of course, a much higher velocity than second sound.

Superconductivity

The phenomenon of superconductivity, discovered in 1911 by Onnes, has proved exceptionally difficult to understand from a theoretical viewpoint. This was perhaps understandable at the time when the simple Drude-Lorentz theory of metals was the only mechanism available, but with the discovery of the wave nature of the electron the situation appeared much more hopeful. Thus the quantum theory of solids, developed in the thirties, enables us to understand at least qualitatively, for example, why carbon atoms in a graphite lattice constitute quite a good electrical conductor whereas the same atoms in a diamond lattice constitute an excellent insulator—a fact virtually ununderstandable with the classical model. Despite these hopes, however, the quantum mechanical model of the solid state has not, until very recently, proved of any greater value for this problem than its classical predecessor.

Since the discovery of the effect a vast amount of empirical work has, of course, been done and certain, seemingly significant, facts have emerged. Among these may be mentioned the following:

(*a*) No monovalent metal has ever been found to be a superconductor.

(*b*) Although known superconductors have a wide variety of crystal lattice structures there nevertheless appears to be a connection between the occurrence of the effect and the lattice structure. Thus "white" tin (tetragonal) is a superconductor while "grey" tin (diamond type) is not.

(*c*) The transition into superconductivity invariably occurs at a low temperature, i.e., 20°K. or below.

(*d*) At any temperature below the transition superconductivity may be destroyed by applying an appropriate magnetic field whose magnitude is a unique function of the temperature for a given super-

conductor (threshold curve). Further, transitions across this threshold are thermodynamically reversible.

(*e*) In general, for time invariant fields the electric vector **E** everywhere within the metal, while in the superconducting state, is rigorously zero (Onnes effect). The same is true for the magnetic vector **B** except for a thin surface layer of the material of the order of 10^{-5} cm. deep. Within this layer the magnetic field at the surface decays, exponentially, to zero (Meissner effect).

(*f*) Measurements of the resistance in the superconducting state at very high frequencies ($\backsim 10^3$ megacycles/sec. and higher) indicate that only a fraction of the conduction electrons are in a state capable of supporting resistanceless flow ("superfluid" electrons). The fraction of such electrons increases monotonically from zero at the transition temperature to unity at absolute zero.

It is a consequence of (*d*) and (*e*) above that the entropy of the system in the superconducting state is less than that in the normal state, i.e., the superconducting state must be one of higher thermodynamic order. Now all attempts to detect a change in order in the ionic lattice in passing into the superconductive state have failed and one must therefore suppose that the ordering is electronic and probably in momentum space. The question, therefore, arises as to what mechanism can be imagined which might produce such an effect, and some recent work both on the experimental and theoretical side appears to have provided some indications of the answer.

Working independently, Reynolds, Serin, Wright & Nesbitt (25) and Maxwell (26) have shown experimentally that the transition temperature of superconducting mercury depends on the isotopic mass. Many years previously Onnes had searched for a similar effect in natural lead and in lead derived from natural radioactive decay, but with negative results. It is probable, in the light of the new experiments, that an effect in lead occurs; it was probably masked by impurities since superconductive measurements are sensitive to these. The work on mercury made use of material supplied by the separated isotopes program recently inaugurated at Oak Ridge. These measurements, in effect, determined the threshold curves for several samples of mercury of different atomic mass number using the disappearance of the Meissner effect, at various fields and temperatures, as the criterion. There is little doubt but that a real dependence of the transition temperature (T_o) upon the ionic nuclear mass is present. In a second paper, Serin, Reynolds & Nesbitt (27) redetermine (T_o) for the same group of isotope samples used previously and with results only slightly at variance with their first ones. In this later paper they also point out that the product $T_o M^{1/2}$, where M is the average nuclear mass, is remarkably constant.

In Table IV the results of all three experiments are reproduced, the two separate determinations of Reynolds *et al.* being designated as Run I and Run II, respectively. In computing the product $T_o M^{1/2}$ the results of Run II

TABLE IV

SUPERCONDUCTING MERCURY ISOTOPES

Observer	Average Mass (M)	Transition Temp. (T_o)		$T_oM^{1/2}$
		Run I	Run II	
Reynolds *et al.*	203.4	4.126	4.137	58.99
Reynolds *et al.*	202.0	4.143	4.147	58.93
Reynolds *et al.*	199.7	4.161	4.167	58.88
Maxwell	198	4.177	—	58.78
Maxwell	200.6	4.156	—	—
Reynolds *et al.*	200.7	4.150	4.154	58.84

are employed since the authors probably feel that these are the more accurate.

In a later communication Maxwell (28) has extended this work to isotopes of tin, wherein a similar effect has been observed. Although only natural tin ($M=118.7$) and one enriched sample containing about 83 per cent Sn^{124} were observed, the product $T_oM^{1/2}$ appears to be constant for this element also.

On the other hand, Herzfeld, Maxwell & Scott (29) have pointed out that the function $M^\alpha T_o = C$ is comparatively insensitive to the value of the exponent α. Using a plot of log T_o *versus* log M they find that the best least squares fit of the experimental data to the resulting straight line yields a value $\alpha = 0.378 \pm 0.021$. They point out that the exact value of α is a matter of some importance in interpreting, theoretically, the meaning of the experiments. The spread in transition temperatures for the various isotopic masses is, of course, very small and, accordingly, in determining the correct value for α great experimental precision is required. It appears that the experiments quoted above lacked sufficient precision to enable one to decide, with any degree of certainty, between the values $\alpha = 0.500$ and $\alpha = 0.375$.

Accordingly Serin, Reynolds & Nesbitt (30) have re-examined the matter experimentally in an attempt to improve the accuracy. In particular, they have taken precautions to minimize strains in their specimens since it has long been known that a strained superconductor has a slightly different transition temperature than an unstrained specimen. In addition to their original samples, they have added three new ones of different isotopic constitution, making a total of seven samples in all. These results are shown in Figure 13 which is self-explanatory.

In their original work Serin, Reynolds & Nesbitt, assuming the correctness of $\alpha = 0.500$, pointed out that, inasmuch as the Debye characteristic temperature, Θ, is proportional to the maximum frequency of lattice vibrations

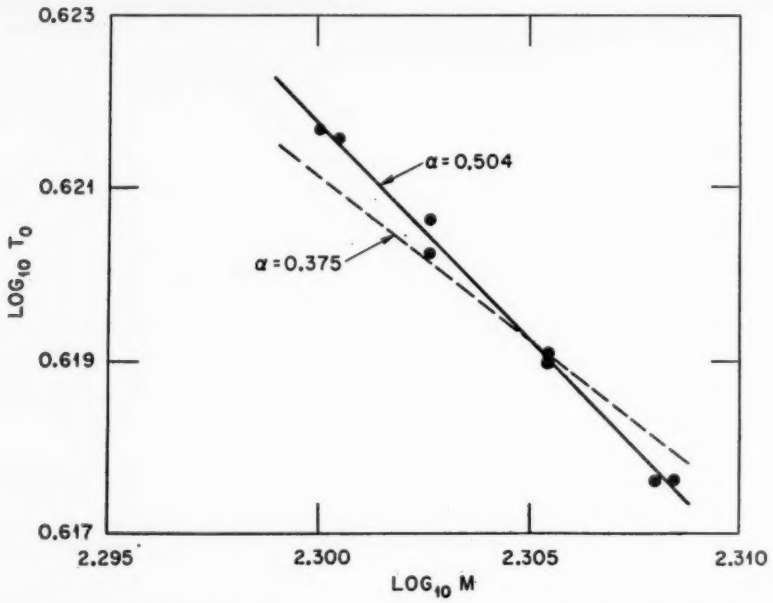

FIG. 13. The relation between the superconductivity transition temperature and the average nuclear mass for several mercury isotopes [after Serin, Reynolds & Nesbit (30)].

(ν_{max}), and since, of course, $\nu_{max} \sim 1/\sqrt{M}$ it follows that $T_o/\Theta = \text{constant}$ for $\alpha = 0.500$.

The above, if true, must of course be regarded as no more than an empirical fact with the mechanism involved yet to be disclosed, and two approaches, of a not entirely dissimilar nature, have been proposed, by Bardeen (31) and Foehlich (32), respectively.

It will be recalled that the superconducting state represents, thermodynamically, a more ordered state than the normal one and presumably such ordering takes place in the p-space of the electrons. In addition, the transition into superconductivity has, so to speak, two separate aspects. Thus (*a*) upon becoming superconducting a metal loses all resistivity as measured by a time invariant electric field, and (*b*) upon entering the superconducting state the magnetic permeability vanishes (apart from a thin surface layer), i.e., becomes diamagnetic with a maximum possible susceptibility. The time gap between the discovery of (*a*) and (*b*) was about 20 years and the earlier theories had all attempted to handle case (*a*), i.e., to regard superconductivity as a limiting case of normal metallic conductivity wherein the conductivity became infinite. Such attempts met with no success whatever and indeed a very general quantum mechanical theorem by Bloch showed that no system of persistent currents could be stable, i.e., yield a minimum in the energy

of the system. After the discovery of effect (*b*), London suggested a way out of this dilemma by picturing a superconductor as a "large diamagnetic atom" which would yield the required magnetic properties and, of course, at the same time possess the required persistent current, which is maintained by the (time invariant) magnetic field, either external or produced by the current itself. Bloch's theorem was then avoided since it applies only to systems without electric fields.

Bardeen's treatment, which, in some particulars, is a modification of an earlier approach of Slater is via effect (*b*). In essence, he attempts to show that, as a consequence of interaction between the conduction electrons and the zero-point vibrations of the lattice, a large diamagnetism is produced which is identified with superconductivity. That some sort of electronic coupling is necessary if a metal is to exhibit the large diamagnetism necessary to superconductivity had originally been postulated by London. Thus the effect of a magnetic field on an assembly of free electrons would give rise only to a very weak diamagnetism; but with coupling of such a nature that the lowest states are separated by a finite interval from excited ones a large diamagnetism becomes possible. Also, as Slater has shown, in order to obtain diamagnetism comparable to a superconductor (susceptibility $\chi = -1/4\pi$) the electronic wave functions would have to extend over approximately 137 interatomic distances ($\sim 10^{-6}$ cm.), provided an applied magnetic field did not exceed $\sim$1,400 gauss. With wave functions spread over lesser or greater distances than this only a feeble diamagnetism results, i.e., that shown by single atoms in former case or a gas of free electrons in the latter. Bardeen proceeds from this point by pointing out that a displacement of lattice ions from their equilibrium position, which are coherent over distances $\sim 10^{-6}$ cm., will give a lower energy for electrons than coherence over larger or smaller distances, and, further, a lower energy than they would possess in the case of a noncoherent or "normal" (i.e., nonsuperconductive) state. Interaction between such coherent lattice modes and electrons are shown to give rise to new electronic states which are linear combinations of the wave functions with the energy near the Fermi surface and which have energies differing by ΔE from the normal states. If this interaction is of such a nature as to depress the levels just below the Fermi surface and raise those above there will be a net decrease in electronic energy if

$$\Delta E \sim kT.$$

Bardeen assumes therefore that

$$\Delta E \sim kT_o$$

and proceeds to consider a volume V containing a small number of states p. It is necessary to consider a small V since the amplitude of the zero-point motion varies as $V^{-1/2}$, but if this volume is too small the wave functions of the electrons cannot be confined to the required region of coherence without an increase in Fermi energy.

For an arrangement with zero-point energy (in volume V)

$$\tfrac{1}{2}h\nu = \tfrac{1}{2}k\Theta$$

and it follows from resistivity theory that

$$kT_o \sim \Delta E \sim \left(\frac{\Theta N(E)}{2Tp}\right)\left(\frac{e^2}{3\pi\hbar}\right)\left(\frac{dE}{dk'}\right)\sigma$$

where $N(E)$ is the state density in range ΔE, k' the wave number, and σ the electrical resistivity, assuming σ/T is a constant. The result shows T_o proportional to Θ as experiment seems to require.

A rough estimate of T_o may be found from this by expressing $N(E)$ and dE/dk' in terms of the density of valence electrons (n_e) in the free electron approximation. This gives

$$T_o \sim \left(\frac{\hbar e^2}{4\pi m}\right)\left(\frac{\Theta\sigma n_e}{kTp}\right)$$

which has the right order of magnitude for superconductors such as Hg or Sn provided $p \sim 10$–20 and $n_e = 10^{23}/\text{cm}^3$.

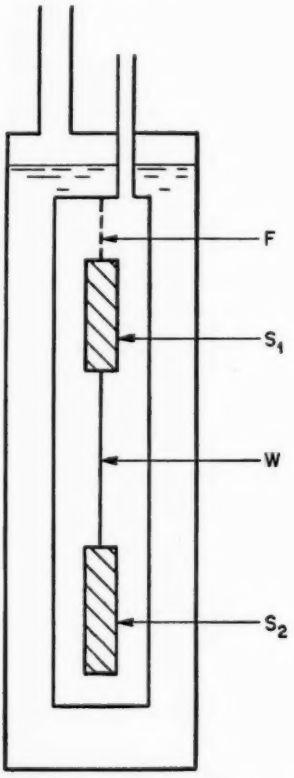

FIG. 14. Schematic of apparatus used for two-stage adiabatic demagnetization [after Darby, Hatton & Rollin (35)].

Ultra Low Temperatures

The vapor pressure of liquid helium is approximately 10^{-3} mm. Hg at 0.66°K.—that is to say, already a high vacuum. The only practical method which has so far been devised to achieve temperatures much below this is the process of demagnetizing a magnetic salt starting from a temperature, produced with liquid helium, of the order of 1°K.[5] This powerful method was first suggested, independently, by Debye and Giauque in 1926.

Recently deKlerk, Steenland & Gorter (34) have reported a new record for low temperatures so produced, namely, 1.5×10^{-3}°K. The salt used was a powdered mixed crystal of chromium alum and aluminum alum containing about 1 part Cr to 20 parts Al.

The salts used in this kind of work generally have a "specific heat anomaly" at some low temperature depending on the salt. That is to say, the specific heat has a sudden high peak superimposed on the Debye curve. This clearly acts as a "barrier" to the achievement of any much lower temperature than that at the point where this anomaly occurs. With the above mixture, however, this barrier had not been reached even at the lowest temperature quoted above.

A most notable advance in the technique of adiabatic demagnetization has recently been reported by Darby, Hatton & Rollin (35). In general, demagnetization experiments are carried out, e.g., from initial condition $T_o \sim 1$°K., $H_o \sim 20{,}000$ gauss to final conditions $H_f \sim 0$, $T_f \sim 0.01$°K. or less. In other words the process has been, up to now, "one shot" or single-stage. The above authors have now shown that a two-stage process is practical. Figure 14 shows, schematically, their apparatus. (S_1) and (S_2) are two magnetic salts connected by a wire (W) of pure lead, the whole assembly being suspended by an insulating fiber (F) in a container surrounded with liquid helium in the usual way. Both salts are brought to ~1°K. by heat exchange with the bath and then adiabatically isolated by pumping the exchange gas from the container, a magnetic field of ~4,000 gauss being maintained on both salts, and the wire. The magnet is now lowered so that (S_1) is demagnetized, while (W) and (S_2) remain in the field. Since this field far exceeds the superconducting threshold for lead the wire remains in the normal state. Now it is known that the thermal conductivity of a pure superconductor is much larger in the normal state than in the superconducting phase. Hence heat is transferred from (S_2) to (S_1). If now the field on (S_2) is removed two things occur. First (S_2) falls to a much lower temperature still and second, W becomes superconducting (i.e., its thermal conductivity becomes greatly reduced). Hence S_2 is effectively thermally isolated from the hotter stage (S_1), the wire W acting as a "heat switch" in the process.

With a field of only 4,200 gauss the end temperature reached by S_2 was ~0.01° Curie, which is near the limit imposed by the specific heat anomaly

[5] The vapor pressure of pure He^3 at about 1°K. is ⌣10 mm. Hg. as against ⌣0.1 mm. Hg. for He^4. Should He^3 become available in usable quantities (⌣several liters S.T.P.) this would be another possibility. [See reference (33).]

for the salt used. This technique should bring the whole field of very low temperatures within the scope of cryogenic laboratories not equipped with large electromagnets.

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PROGRESS IN METALLURGY

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In the preparation of the chapter on metallurgy, the authors were confronted with a difficult problem of selection. As the atomic energy program includes in one way or another a considerable fraction of all of the metallic elements, an adequate survey of the year's accomplishments would require a volume for metallurgy alone. Condensation in one chapter has not permitted even the listing of all of the excellent papers that appeared during the year. In view of this limitation, it has appeared wise to confine the discussion to a few of the developments that seem likely to be of interest to the greatest number of readers.

To be more specific, we have listed below the six fields of which we propose to make a high-light review: (*a*) the effect of nuclear irradiation on the properties of metals, (*b*) new measurements on the physical properties of the fissionable metals, thorium and uranium, (*c*) data on the alloys and compounds of thorium and uranium, (*d*) the application of radioisotopes to metallurgical investigations, (*e*) newly published information on three metals of interest in reactor design, and (*f*) a very brief abstract of reports on liquid metals that could be considered usable in heat exchangers.

The material included has been taken from original papers only, but the review is not a critical one in the sense that an attempt has been made to judge the accuracy of the data. No historical background could be presented because of the exigencies of space. For this, the interested reader is referred to the various scientific, metallurgical, and engineering indexes and especially to volumes 14B and 19B, Division IV, of the National Nuclear Energy Series [references (53) and (47), respectively.] The *Liquid-Metals Handbook* (37) contains much useful and recent information. The bibliography has been restricted mainly to work published in 1950, but not all of the papers that contained original data could be included.

The Effects of Irradiation

The ability of neutrons to knock atoms out of their lattice sites or even to convert them to atoms of a different element and thus produce alloying might be expected to produce measurable effects on the properties of a metal. This expectation has been realized in experiments like those of Billington & Siegel (11), who subjected several metals and alloys to neutron bombardment in a reactor and measured the change in properties, particularly in hardness and electrical resistivity.

Unalloyed aluminum and copper showed almost no change in resistivity as the result of irradiation, and aluminum experienced little change in hard-

ness. By contrast, annealed copper showed some hardening after short exposures and under the relatively large exposure of 5×10^{19} neutrons per sq. cm. of cross-section, increased from F43 to F90 on the Rockwell hardness tester. Cold-worked copper increased only from F93 to F97 under the same treatment.

Much more striking effects were observed in some alloys. Irradiation of an ordered copper-gold alloy having a composition corresponding to Cu_3Au produced the relatively large increases indicated in Table I, which shows the change in resistivity in microhm-cm. for initially ordered and initially disordered specimens subjected to increasing neutron irradiation. The considerable increase in resistivity of the initially ordered specimens is attributed to the disordering action of the irradiation which may be assumed to have knocked many of the atoms out of their ordered positions. The slight increase in resistivity of the initially disordered specimens, according to the authors, probably is caused by the formation of mercury atoms as the result of neutron capture and subsequent decay.

TABLE I

THE CHANGE IN THE RESISTIVITY OF COPPER-GOLD ALLOYS, OF COMPOSITION Cu_3Au, BY IRRADIATION

Total flux, neutrons/cm.$^2\times10^{19}$	Resistivity of specimens (microhm-cm.)			
	Ordered		Disordered	
	before	after	before	after
0.4	4.60	5.71	11.20	11.25
0.6	4.60	6.25	11.20	11.25
1.0	4.60	7.54	11.20	11.17
1.5	4.60	8.36	11.20	11.21
3.3	4.60	10.10	11.20	11.30

An age-hardening copper-beryllium alloy containing 2.15 per cent beryllium was subjected to irradiation in the quenched, aged, and overaged conditions. For irradiation with 4×10^{19} neutrons/cm.^{2} samples showed the changes in resistivity indicated in Table II. Specimens that were reduced 50 per cent by cold-rolling after being quenched, but before being aged, experienced much less change than those included in the table.

Hardness changed in an equally striking manner. Exposure to an irradiation of 9×10^{19} neutrons/cm.^{2} produced the changes shown in Table III. The changes in resistivity and hardness appear to be the direct result of action by neutrons and are not a secondary heating effect. For example, the resistance of an age-hardened copper-beryllium alloy decreases if heated, but increases if irradiated.

Heating removes the effects of irradiation. Thirty seconds at 350°C. sufficed to restore the two alloys above to their former condition.

TABLE II

THE EFFECT OF IRRADIATION ON THE ELECTRICAL RESISTIVITY OF A COPPER-BERYLLIUM ALLOY CONTAINING 2.15 PER CENT BERYLLIUM

Heat Treatment			Resistivity		
Quenching temp., °C.	Aging temp., °C.	Aging time *min.*	Before irrad. *microhm-cm.*	After irrad. *microhm-cm.*	Change, *per cent*
800	tested after quenching		234.5	273.4	15.5
800	220	100	238.3	251.8	5.5
800	310	100	200.0	211.5	5.8
800	400	240	130.0	143.1	9.4
800	550	1080	165.3	192.2	14.5

Irradiation with α-particles also affects the electrical resistivity of metals according to Martin (38) who made measurements on metals maintained at −150°C. during irradiation in a cyclotron. The resistivity of aluminum increased by 38 per cent because of the irradiation. Copper increased in resistivity by 32 per cent. Ordered AuCu increased in resistivity by 235 per cent and ordered $AuCu_3$ by 200 per cent. On the other hand, the disordered alloys changed only slightly. Upon returning to room temperature after bombardment, the elemental metals returned to normal resistivity but, as might be anticipated, the ordered alloys retained a considerable fraction of

TABLE III

THE EFFECT OF IRRADIATION ON THE HARDNESS OF A COPPER-BERYLLIUM ALLOY CONTAINING 2.15 PER CENT BERYLLIUM

Heat Treatment			Hardness, Rockwell G Scale		
Initial Treatment	Aging		Initial	Final*	Change
	Temp., °C	Time, *min.*			
Quenched from 775°C.	(tested after quenching)		18	80	62
Quenched, cold-rolled 50%	(tested after rolling)		83	95	12
Quenched, cold-rolled 50%	285	30	94	98	4
Quenched, cold-rolled 50%	285	60	101	102	1
Quenched, cold-rolled 50%	285	120	100	103	3
Quenched, cold-rolled 50%	285	180	103	104	1
Quenched, cold-rolled 50%	395	60	89	95	6
Quenched, cold-rolled 50%	400	1,080	67	85	18

* After 9×10^{19} neutrons/cm^2.

their increase. Also, the alloys retained a considerable fraction of the change in temperature coefficient of resistivity and in lattice parameter. All specimens except aluminum showed an increased hardness as the result of irradiation.

Yockey, Jeppson & Keen (65) studied the rate of creep of aluminum wire while it was being bombarded in a cyclotron. The wire was allowed to creep at a constant elevated temperature and constant load with the cyclotron not in operation for a period long enough to reach the second stage of creep. When the rate of creep was established, the cyclotron beam was turned on. While maintained at the same temperature, the specimen was irradiated for a sufficient time to permit measurements of the creep rate under the changed condition. The effect of alpha particle bombardment on the rate of creep of 0.013-inch diameter aluminum wire under a stress of 900 psi at 340°C. was to decrease the rate of creep by a factor of three. The beam current during the tests was 3.5 μamp./cm.^{2}.

Measurements of the Physical Properties of Uranium and Thorium

Additional information on the physical properties of uranium and thorium continues to be released into the open literature. From a study of single crystals that were retained in an alloy containing 1.4 per cent chromium when it was cooled rapidly from 720°C., Tucker (60) has proposed a structure for β-uranium based on single crystal data. This phase, which has been unusually difficult to analyze, has a tetragonal unit cell with $a_o = 10.52$ Å and $c_o = 5.57$ Å. It contains 30 atoms, probably arranged according to the space group C_{4v}^4. The atoms are in layers parallel to the $a_o b_o$ plane at heights of $1/4\ c_o$ and $3/4\ c_o$. In the layers the atoms have positions similar to those in the basal plane of a close-packed hexagonal substance, but the atoms at the center of some hexagons have been displaced by a distance of about $1/4\ c_o$ in the c_o direction, that is, to positions about midway between the planes. This structure is the same as that reported by Shoemaker (55) for the sigma phase, FeCr.

A recently published report on the melting point of uranium states the temperature to be 1,090°C. The work was done by Allendörfer (3) at the Deutschen Gold- und Silber-Scheideanstalt in 1942 but not published until 1950. The determinations were made with a platinum/platinum-rhodium thermocouple immersed within a protecting tube in a mass of 245 g. of uranium. The uranium had been distilled from a less pure metal and deposited on a uranium cooling tube. After the measurements had been finished, the uranium was analyzed with the result (in percentage) shown below:

uranium	iron	silicon	aluminum	beryllium
99.96	0.01	0.02	0.00	trace

The average of three determinations on heating was 1,089°C. and of three determinations on cooling was 1,094°C. Allendörfer stated his final value as 1,090° ± 2°C. The discrepancy between this result and the obviously careful measurements of Dahl & Cleaves (19) is difficult to reconcile. However, it may be said that the somewhat scattered values from the Manhattan project literature favor the figure of Dahl & Cleaves.

During his investigation Allendörfer observed that the boiling temperature of uranium at 10^{-3} to 10^{-4} mm. Hg pressure was in the vicinity of 1,450° to 1,500°C.

Measurements on the superconductivity of uranium have been published by Goodman & Shoenberg (23). Shoenberg (56) previously had been unable to observe superconductivity down to 1.08°K. but repeated his experiments on new samples after Alekseyevsky & Migunov (2) reported that their specimens had shown superconductivity at 1.3°K. Of three samples that Goodman & Shoenberg tested, one became superconducting at 1.3°K. but the other two showed no evidence of change at that temperature. However, these two could be made superconducting if their temperatures were reduced to 0.75°K. by adiabatic demagnetization. In all cases the transition was not sharp but extended over a range of 0.2°K. The authors suggested that contaminating substances were responsible for the variation in behavior but observed that the specimen which become conducting at 1.3°K. contained more contaminating elements than the two that did not.

The magnetic properties of uranium were studied by Bates & Mallard (8). The metal contained 700 p.p.m. of iron, 60 p.p.m. of nickel, and 5 p.p.m. of cobalt, but tests of the susceptibility at increasing field strength did not indicate ferromagnetism. The susceptibility changed with temperature according to the graph in Figure 1.

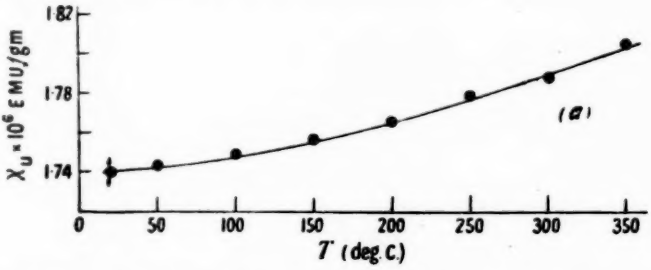

FIG. 1. The change in magnetic susceptibility of uranium with temperature (8).

Finniston, Jones & Madsen (22) studied the Meyer hardness of uranium, particularly with respect to the variation of the ultimate ball hardness P_u and the exponent n in the harness equation. P_u is the force required to sink the indenting ball into the metal for half its diameter divided by the area of the impression, and n is an exponential constant that depends on the nature of the metal and its mechanical condition but is independent of the diameter

of the ball. For all cubic metals, P_u decreases as n increases, but for α-uranium and several other noncubic metals, P_u and n increase together. Some preliminary tests on gamma uranium indicated that it followed the usual relationship for cubic metals.

Information on the elastic constants of uranium has been published by Laquer, McGee & Kilpatrick (36) who determined Young's modulus and the shear modulus by dynamic methods. They used specimens prepared in three different ways as indicated in Table IV which gives their results. The authors estimate an accuracy of 1 per cent for Young's modulus and 0.5 per cent for the shear modulus. From averages of values in the table, they calculated the value of the bulk modulus to be 12.6×10^{11} dynes/cm.^{2} but state that the accuracy is not greater than 10 per cent. Over a 10°C. range of temperature, they determined the temperature coefficient of Young's modulus to be $dE/E\ dT=5\times10^{-4}$ per degree C. and to be negative.

TABLE IV

THE ELASTIC CONSTANTS OF URANIUM

Specimen	Density gm./cm.^{3}	Young's modulus dynes/cm.^{2} $\times10^{-11}$	Shear modulus dynes/cm.^{2} $\times10^{-11}$	Poisson's ratio
Swaged, ann.	18.98	20.05	8.20	0.22
Extruded*	18.94	20.17	8.27	0.22
Extruded*	18.94	20.92	8.35	0.25
Cast	18.98	20.70	8.35	0.22
Cast	18.98	20.5	8.34	0.24

* Extruded in gamma condition.

Both uranium and thorium can be produced in powder form for use in powder metallurgy. The method takes advantage of the hydride forming properties of both metals as described in a summary by Chiotti & Rogers (16) of work done by a number of investigators. As an illustration, the production of powdered uranium will be described briefly.

Hydrogen combines directly with massive uranium at temperatures below 100°C. and the reaction becomes energetic at 225°C. If the hydride is then heated above 430°C., the pressure of hydrogen exceeds atmospheric value as indicated in Figure 2, and the hydrogen may be pumped off readily. During the formation of the hydride the material disintegrates to a powder and this form is retained during the dissociation step. Both the hydride and the powdered metal may ignite spontaneously in air.

Uranium at elevated temperature provides a simple means of purifying hydrogen. It combines readily with oxygen and nitrogen but allows the hydrogen to pass on without reaction.

Thorium behaves in a similar manner but as it forms two hydrides, of

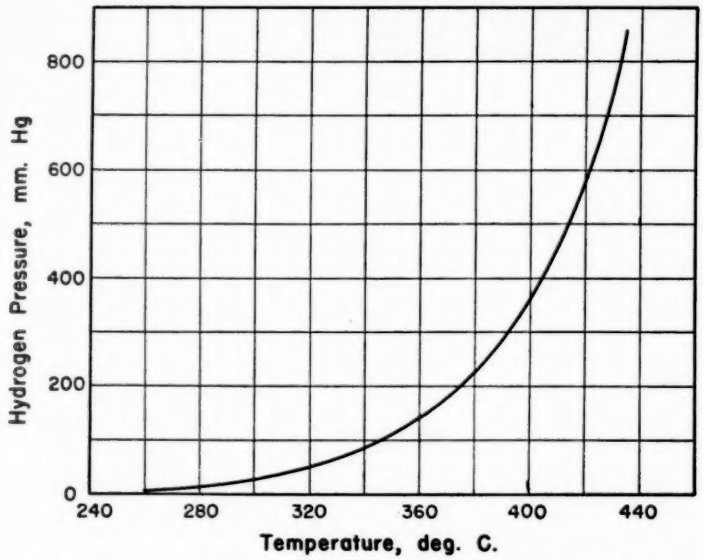

FIG. 2. The increase in dissociation pressure of uranium hydride with increasing temperature (16).

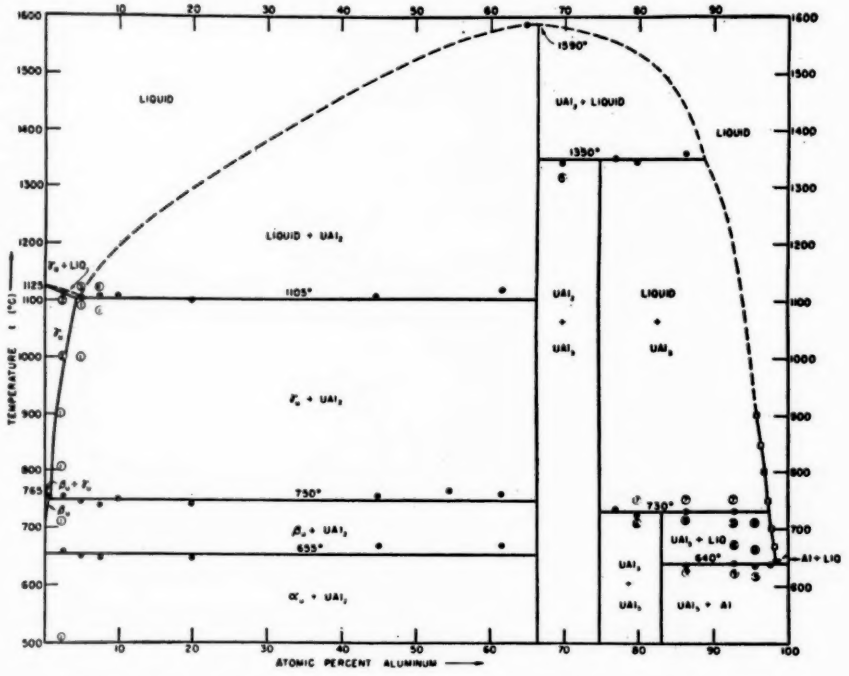

FIG. 3. The constitutional diagram of the uranium-aluminum alloys (24).

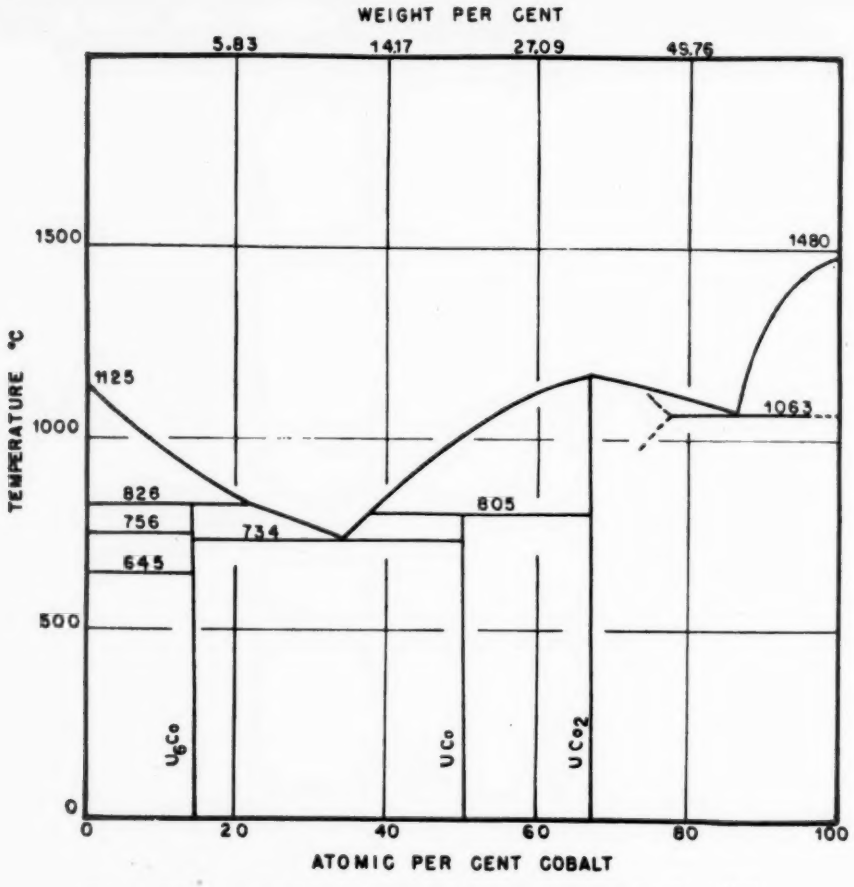

FIG. 4. The constitutional diagram of the uranium-cobalt alloys (43).

which the higher appears to be ThH_4, a two-step operation is required for forming the hydride and also for dissociating it.

The availability of a small amount of polonium provided an opportunity for Maxwell (39) and Beamer & Maxwell (9) to determine some physical properties of the element. As the investigators were obliged to work with very small deposits of metal which were being converted rapidly to lead by radioactive decay, they did not claim high accuracy for their results.

Polonium has a melting point of about 250°C. and a density of 9.4 ± 0.5 gm./cm.^{3}. It exists in two allotropic modifications of which the lower temperature one is called alpha and the upper, beta. Transformation from one to the other takes place with extensive hysteresis. α-Polonium in thick deposits is converted to β-polonium in the range from 65°C. to 85°C., at higher temperatures for thin deposits though the reverse change does not occur until the specimen approaches room temperature. The films of polonium are de-

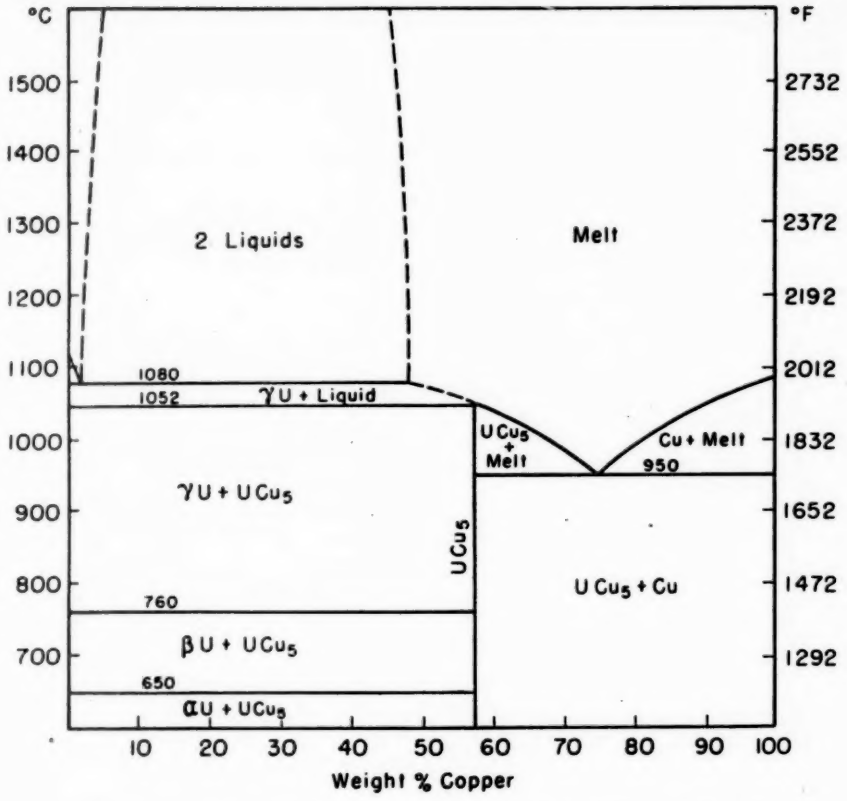

FIG. 5. The constitutional diagram of the uranium-copper alloys (62).

posited as β metal. Upon being cooled to room temperature they change to the α modification over a period of 10 to 15 hr. The α form has a simple cubic cell with a parameter of 3.345 ± 0.002 Å. The β modification is simple rhombohedral with a parameter of 3.359 ± 0.002 Å and an angle of 98° 13′ $\pm 3'$.

Both forms of polonium have an electrical resistivity of 40 to 45 microhm-cm. with a possible error of several microhm-cm. The temperature coefficients of resistance are quite different as the alpha form has 4.5×10^{-3} ohm/ohm/deg. C. and the beta has 7.0×10^{-3} ohm/ohm/deg. C. Polonium and lead appear to form a solid solution up to 50 per cent lead, at least.

ALLOYS AND COMPOUNDS OF THORIUM AND URANIUM

Alloys.—Constitutional diagrams of several alloys of uranium were published in the open literature during the year. These can be described most satisfactorily by reproductions of the diagrams. In most instances, the investigations were carried out during the war years but the reports have re-

mained secret until comparatively recently. Little comment on these diagrams is required.

The uranium-aluminum system in Figure 3 is the result of an investigation made in 1943 by Gordon & Kaufmann (24) but not published in a technical journal until 1950. The diagram of the uranium-cobalt alloys, Figure 4, has been declassified from a classified report (43). Uranium and copper have the diagram shown in Figure 5 which is quite simple except for a two-liquid region that exists to relatively high temperatures. The report on this system was published by Wilhelm & Carlson (62) long after the work was done.

Figure 6 exhibits the uranium-iron system as drawn by Gordon & Kaufmann (24). An investigation by Grogan (25) arrived at a diagram with the same main outlines. However, Grogan's diagram does not show the solubility of iron in uranium above 815°C. and omits altogether any indication of the A_3 and A_4 transformations in iron.

The uranium-manganese system shown in Figure 7 is another of those studied by Wilhelm & Carlson (62). It is incomplete in that it takes no account of the effect of uranium on the two upper transformations in manganese and remains generally uncertain on the manganese side.

Pfeil (46) worked out the uranium-molybdenum system to about 60 per

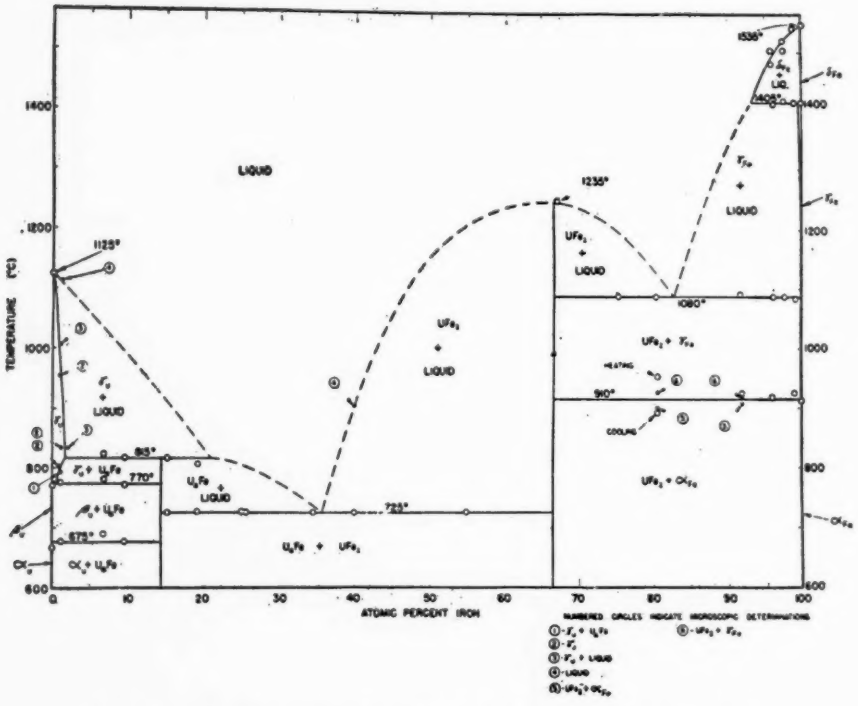

FIG. 6. The constitutional diagram of the uranium-iron alloys (24).

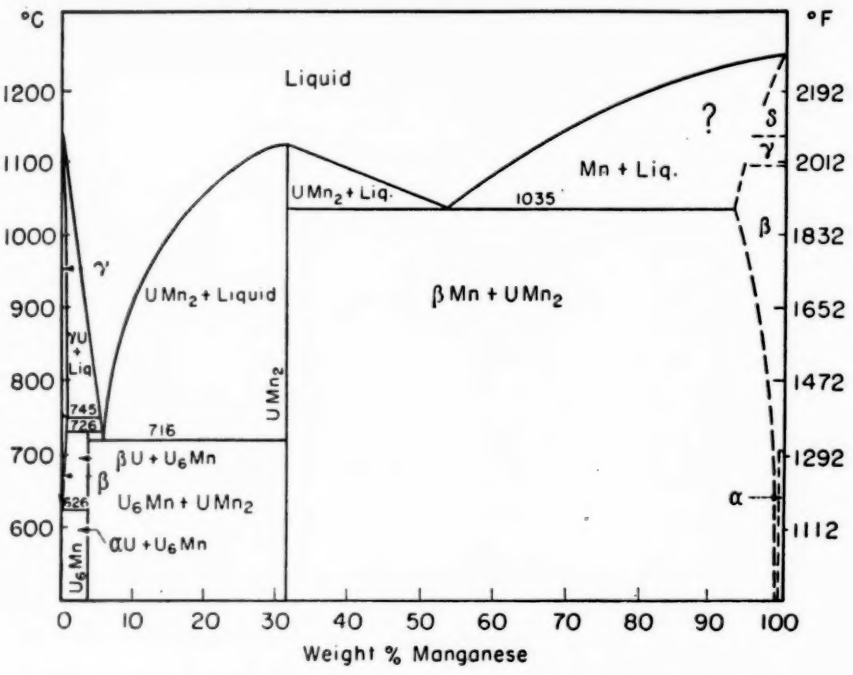

FIG. 7. The constitutional diagram of the uranium-manganese system (62).

cent molybdenum. His diagram, which is presented here as Figure 8, has a general similarity to one shown in a classified report (1).

Schramm, Gordon & Kaufmann (52) have published diagrams for the uranium-tantalum and uranium-tungsten systems. These diagrams, shown here as Figure 9 and Figure 10, are similar in character. Neither indicates any solubility of one metal in the other at low temperature and only limited solubility at high temperature.

Of three alloy systems involving thorium that have been worked out since the end of World War II, only the thorium-carbon (63) system is recent enough to be included in this review. It is shown in Figure 11. As nearly as can be determined, all alloys up to about 9.3 per cent carbon solidify as solid solutions but, except for very low carbon contents and over the range from 3.8 to 4.8 per cent carbon, all solid solutions decompose before reaching room temperature.

Compounds.—Additional data on the structure of the compounds formed by the fissionable metals appeared in the scientific literature during the year. Baenziger, Rundle, Snow & Wilson (7) reported on the compounds of uranium with the four metals manganese, iron, cobalt, and nickel. All four of these elements form compounds of the U_6M type. Data on the compounds are presented in Table V. All have four U_6M groups in a body-centered tetragonal cell. The probable space group for the uranium atoms is D_{4h}^{18}.

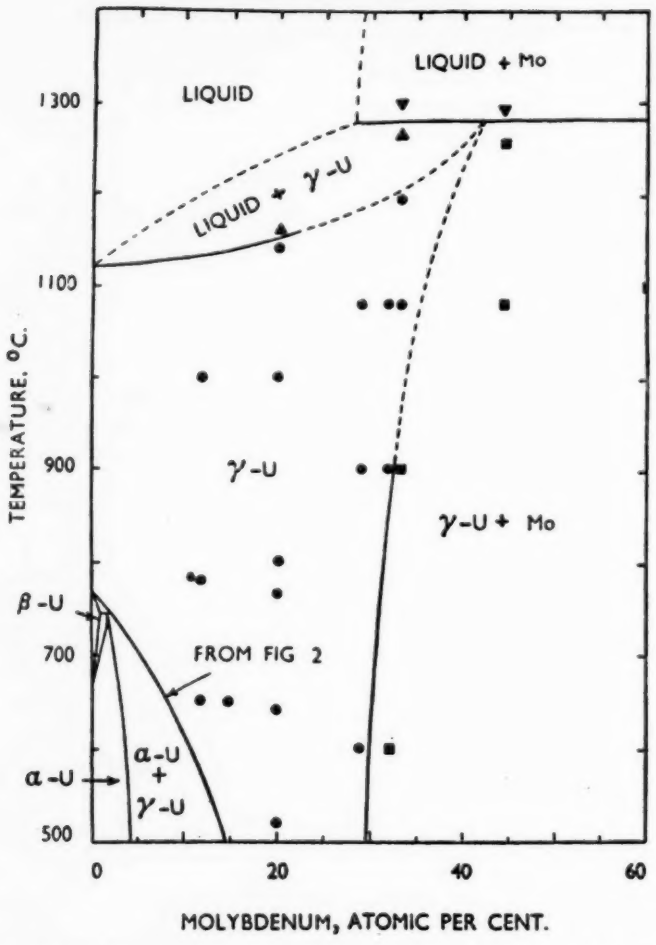

FIG. 8. The constitutional diagram of the uranium-molybdenum alloys (46).

TABLE V

LATTICE CONSTANTS OF THE U_6M COMPOUND

Compound	Cell dimensions, Å		Density gm./cm.^{3}
	a	*b*	
U_6Mn	10.29±0.01	5.24±0.02	17.8
U_6Fe	10.31±0.04	5.24±0.02	17.7
U_6Co	10.36±0.02	5.21±0.02	17.7
U_6Ni	10.37±0.04	5.21±0.02	17.6

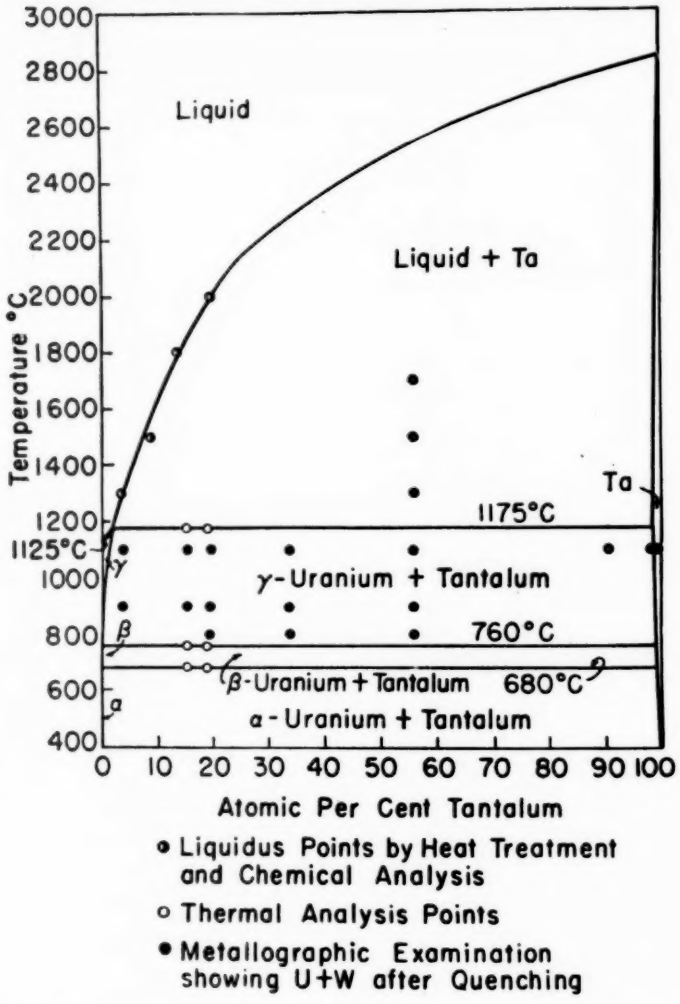

FIG. 9. The constitutional diagram of the uranium-tantalum system (52).

Both cobalt and nickel form compounds of the UM type. The structure of UNi is too complex to be determined from powder patterns alone but UCo has a body-centered cubic lattice with $a_o = 6.3357 \pm 0.0004$ Å and eight UCo groups per unit cell.

Three compounds of the UM_2 were found. They crystallize with a face-centered cubic lattice of which the lattice constants are shown in Table VI. UCo_2 has considerable solubility for cobalt at higher temperatures and undergoes a decrease of lattice parameter as its cobalt content rises.

Nickel forms a compound UNi_5. This compound and the similar UCu_5 are both face-centered cubic. The edge of the UNi_5 cell is 6.7830 ± 0.0005 Å.

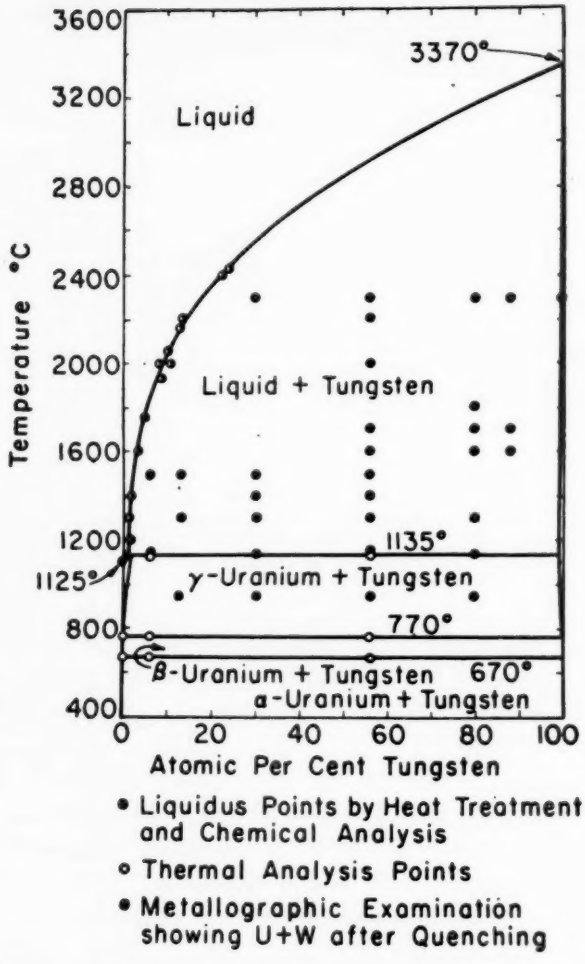

FIG. 10. The constitutional diagram of the uranium-tungsten alloys (52).

TABLE VI

LATTICE CONSTANTS OF THE UM_2 COMPOUNDS

Compound	Cube edge, Å	Density gm./cm.³
UMn_2	7.1628±0.0014	12.57
UFe_2	7.058*	13.21
UCo_2	6.9924±0.0004	13.83

* Value from the literature.

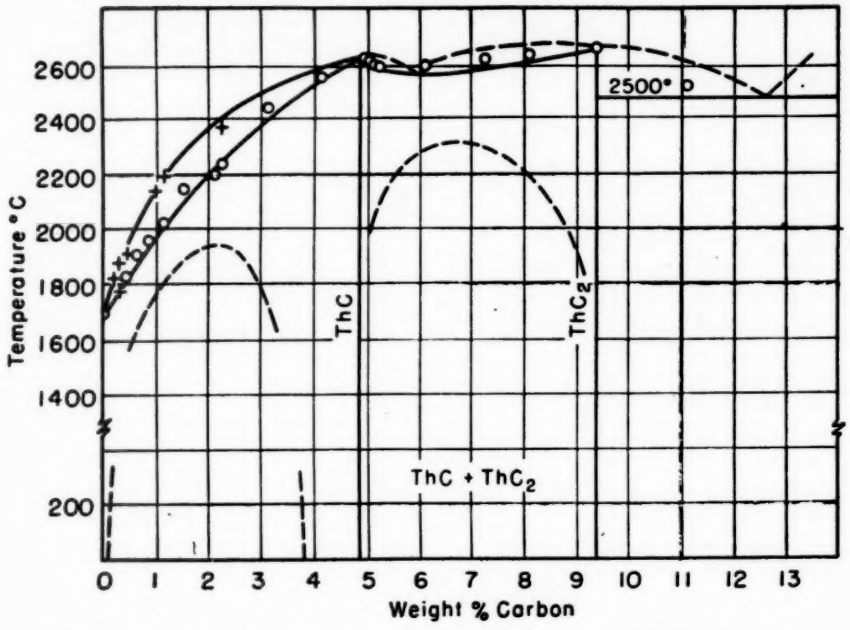

FIG. 11. A tentative constitutional diagram of the thorium-carbon alloys (63).

UCu_5 has sufficient solubility for copper to vary the lattice parameter from $a_o = 7.033 \pm 0.002$ Å to 7.038 ± 0.001 Å.

Additional information on the structure of the borides of uranium and thorium has been contributed by Zalkin & Templeton (66). Their comments concern UB_4 and ThB_4 for which the tetragonal cell dimensions are shown in Table VII.

The space group for the uranium atoms is D_{4h}^5-P4/mbm.[1] These atoms

TABLE VII

LATTICE CONSTANTS OF THREE MB_4 COMPOUNDS

Compound	Cell dimensions, Å			Density gm./cm.³
	a	*c*	*c/a*	
CeB_4	7.205 ± 0.008	4.090 ± 0.005	0.568	5.74
ThB_4	7.256 ± 0.004	4.113 ± 0.002	0.567	8.45
UB_4	7.075 ± 0.004	3.979 ± 0.002	0.562	9.38

[1] P denotes a primitive lattice; 4/m denotes a four-fold rotation normal to a mirror plane; b is a glide-plane with its normal in the a direction and the glide 1/2 b. The final m is a mirror plane with its normal in the direction [110].

are coplanar with each atom having five nearly equidistant neighbors in the plane and two neighbors in adjoining planes at slightly greater distances. The boron atoms fit in among the uranium atoms in three different characteristic groups.

The structure of UBi was described in a report by Brewer, Edwards & Templeton (15). These investigators found that the compound had a sodium chloride type of cell with an edge of 6.364 Å. Compositions in the vicinity of UBi are pyrophoric and the compound can be prepared for analysis only

TABLE VIII

MELTING POINTS, CRYSTAL STRUCTURE AND STABILITY OF SOME COMPOUNDS OF URANIUM AND THORIUM

Compound	Melting point, deg. C.	Crystal Structure*			Stability
		Type	Parameter Å	Calculated density gm./cm.³	
ThN	2,630± 50	NaCl	5.20	11.56	decomposes at room temperature in moist air
ThS	>2,200	NaCl	5.67	9.57	stable in moist air
UN	2,650±100	NaCl	4.880	14.32	attacked slowly by moist air
UC	2,590± 50	NaCl	4.951	13.63	attacked slowly by moist air
UO_2	2,275± 50	CaF_2	5.458	10.96	decomposes slowly under a vacuum at high temperature
US	>2,000	NaCl	5.47	10.9	stable in moist air

* Data from declassified literature.

under thoroughly purified inert gases; otherwise, lines indicating the presence of UO_2 are obtained.

Chiotti (17) investigated the nature of some carbides and nitrides of thorium and uranium for the purpose of finding materials that had valuable properties. His results and some similar data on sulfides by Eastman, Brewer, Bromley, Gilles & Lofgren (20) are presented in Table VIII. Chiotti stated that both carbides and nitrides were converted to oxide if heated in air at 600°C.

APPLICATIONS OF RADIOISOTOPES TO METALLURGICAL INVESTIGATIONS

Applications that have developed as the result of the availability of radioactive isotopes are of two types. The first concerns the use of artificially radioactive substances instead of radium for radiographic work; the second involves the use of tracer techniques in metallurgical studies.

Investigations of radioisotopes as a source for radiography have now settled on cobalt-60 as the most suitable source. Isenburger (31) describes the advantages of cobalt-60 in the following terms:

> . . . the low price and availability of cobalt-60 in greater activities and with comparatively small focal spot size make it possible to radiograph greater thickness of steel, use larger source to film distances, and allow longer exposure times than have been commercially used with radium.

Isenburger's article has an exposure chart for cobalt-60 in terms of radium equivalent.

In a more extensive analysis, Morrison (41) points out that cobalt-60 is the best among the radioactive isotopes when all factors are concerned and that the half life of 5.3 years, corresponding to a decay of 5 per cent in 5 months, is advantageous. It can be obtained readily in amounts equivalent to 2 or 3 gm. of radium and the γ-activity may be made equivalent to 10 mg. of radium per cu. mm. Morrison points out that even with equivalent strength, the exposure times for cobalt-60 may not be the same as for radium, probably because of a difference in response of the film to the different spectra of radiation from the two sources.

Radioisotopes as tracers have proved valuable in several metallurgical applications. In particular, they have been employed in diffusion experiments and in tracing the movement of metals.

An interesting application reported by Pearson, Struthers & Theurer (45) was concerned with the distribution of antimony added to small ingots of germanium to improve the characteristics of the metal as a semiconductor.

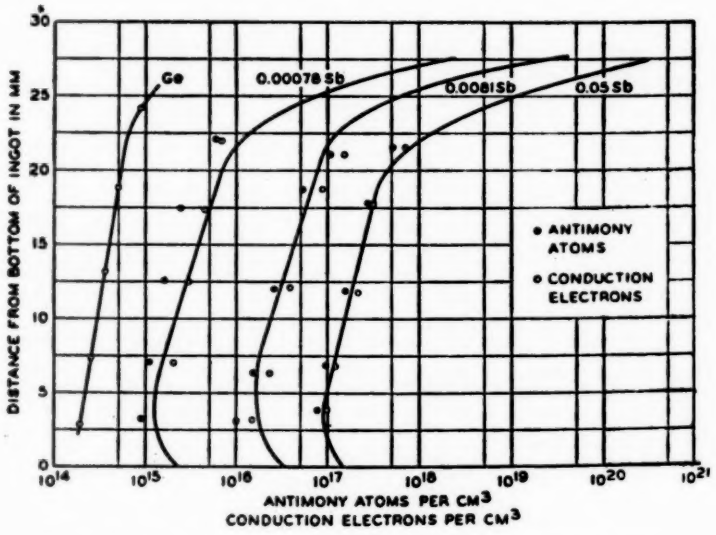

FIG. 12. The distribution of antimony atoms in low-antimony germanium-antimony ingots (45).

As the amounts were too small for satisfactory chemical or spectrographic analysis, antimony-124 was added to a number of melts and the resulting ingots cut into slices which were tested for radioactivity individually. As Figure 12 shows, the antimony content increased with distance from the bottom of the ingot and a considerable proportion of the total addition gathered at the top. The authors noted that the entire exterior of the ingot was relatively high in antimony. The figure shows that the number of antimony atoms per cubic centimeter changes with elevation in the ingot in about the same manner regardless of the percentage of antimony added and that the number of conduction electrons as calculated from measurements of the Hall effect follows the same trend.

Birchenall & Mehl (12) used radioactive iron in a study of the rates of self-diffusion in alpha and gamma iron. As their radioactive material contained in equal amounts both iron-55 with a half life of 4 years and iron-59 with a half life of 44 days they allowed the material to age for about a year so that the iron-59 would not contribute to an uncertainty in counting. They were also obliged, when making measurements in the γ range, to heat and cool their specimens quickly through the upper α range so that the rapid diffusion occurring over that interval of temperature would not influence the results.

In making tests, they plated the active material electrolytically on one side of each of two similar specimens which were then placed with active sides together for the diffusing treatment. The diffusion coefficients were found to be

$$D_\alpha = 2.3 \times 10^3 e^{-23,200/RT}$$
$$D_\gamma = 5.8 \times e^{-74,200/RT}.$$

These coefficients indicate that diffusion is several hundred times as rapid in α-iron as in γ-iron at the same temperature, a fact also evident from the graph in Figure 13.

An illustration of the use of a radioisotope in a determination of vapor pressure is found in Schadel & Birchenall's work (51) on the vapor pressure of silver. These authors added silver-110 to ordinary silver being used in a study of the vapor pressure of the element by the effusion method. The accuracy of their results suggests that counting is a thoroughly dependable method of measuring the weight of metal transferred.

Metals of Actual or Potential Use in Reactors

Among the metals that have been studied because of their potential importance in the production of atomic energy, only beryllium, zirconium, and vanadium will be included in this section.

Beryllium has been produced in metallic form for a number of years but, because of its brittle character, its commercial use has been restricted almost entirely to alloys. However, the element has the very desirable property of slowing down neutrons effectively without capturing them. If it could be obtained as a ductile product, its value would be further enhanced.

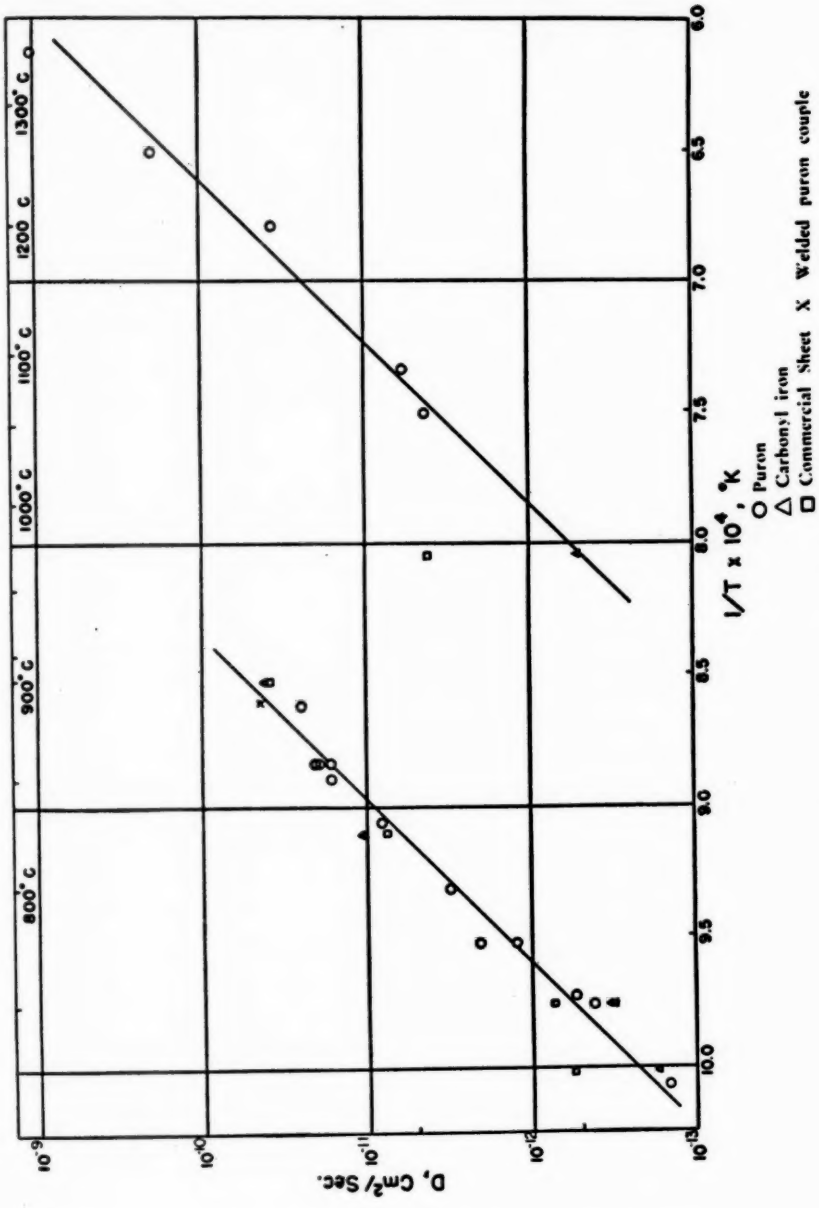

FIG. 13. The self-diffusion of α- (left) and γ- (right) iron (12).

Kaufmann, Gordon & Lillie (33) have summarized the results obtained at the M. I. T. Metallurgical Project during an investigation directed toward producing beryllium in its most usable form. They reduced the impurities to very small percentages—except that they were unable to eliminate oxygen as completely as desirable—but could not produce ductile metal. They were able to extrude rods that showed some elongation in the direction of extrusion but possessed almost no ductility in the perpendicular direction.

The extrusion was performed at temperatures from 815° to 1,090°C. with the beryllium enclosed completely in iron jackets. Rolling operations also were conducted on jacketed beryllium. The operation was successful at any temperature from 370° to 1,090°C. but the higher portion of this range appeared preferable.

The investigators measured a variety of mechanical properties and also the electrical resistivity. They also tried alloying with some 35 metals of which only copper, cobalt, nickel, palladium, and silver showed more than very limited solubility.

The question of an allotropic transformation in beryllium has been discussed by several writers. Recently, Sidhu & Henry (57) presented x-ray evidence in favor of a second allotropic form. Their results have been questioned, however, by Seybolt, Lukesh & White (54) who believe that the lines ascribed to this supposed new form actually are due to BeO.

Zirconium is another metal with a very low tendency to capture neutrons. It is ductile, moderately strong, and has unusual resistance to corrosion. Its production is complicated by the presence of the chemically similar element hafnium in all zirconium-bearing ores. Hafnium has an objectionable tendency to capture neutrons and must be reduced to a very low percentage—a chemical feat of some difficulty. Some success in performing the separation has been achieved, as a survey of very recent chemical literature will reveal.

Metallic zirconium is being produced currently by the hot wire method used by Foote Mineral Company and also by the magnesium reduction process developed by Kroll and carried out by the Federal Bureau of Mines. Developments reported during 1950 were concerned mainly with improvements in the method of production, in testing the metal, and in the preparation and testing of alloys. Kroll, Hergert & Yerkes (35) described apparatus designed to place portions of the magnesium reduction process on a semicontinuous basis. Zirconium tetrachloride from the purifying chamber can be led as a gas by pipes directly to the reaction unit. This unit has devices that permit the introduction of fresh molten magnesium and discharge of salts until the apparatus is filled with sponge zirconium. The authors indicated that substitution of cast iron instead of steel for the magnesium pot permits slightly higher operating temperatures in the reduction furnace and consequently yields a less pyrophoric product. They described also some advantages in adding sodium to the magnesium used as reductant.

The action of several gases on zirconium was studied by Hayes, Roberson & Robertson (28). Details will not be given but all of the gases—carbon monoxide, carbon dioxide, sulfur dioxide, hydrogen, propane, and steam—

caused deterioration of the metal in some ranges of temperature. Sulfur dioxide attacked zirconium only slightly below 500°C. but vigorously at 600°C. Hydrogen begins to combine with zirconium at 400°C. If reaction is allowed to continue long enough, the metal is converted to a brittle hydride. However, the gas can be pumped off at 700°C., and if the reaction has not proceeded too far the zirconium piece becomes ductile again.

Anderson, Hayes, Roberson & Kroll (4) made a series of binary alloys of zirconium with about 20 elements and tested many of them with respect to workability, strength, and resistance to corrosion in air at elevated temperatures. None of the alloys showed good resistance to attack at moderately high temperatures.

Vanadium also has a desirably low tendency to capture neutrons. It has been produced on a pilot plant scale only within the past year. McKechnie & Seybolt (40) described a method for making ductile vanadium by reduction of the oxide with calcium in a bomb but did not give details concerning the properties of the metal. An independent investigation, reported by Kinzel (34), was carried into the fabrication and testing stage. Kinzel states that solid masses of crystalline vanadium weighing several pounds have been produced and worked and that 100 pounds per day of massive ductile vanadium could be produced with the equipment in operation.

Liquid Metals

As nuclear reactors for the production of power require liquid media for transferring heat, designers of these reactors have a strong interest in the properties of liquid metals. Because of this interest, much of the available information, both early and recent, has been collected and published during 1950 as a *Liquid-Metals Handbook* (37). Of importance to metallurgists are the data on the physical, thermal, and chemical properties of the liquid metals. The book gives also the data on the tendency of most of the isotopes of the low-melting metals to capture low energy, or thermal, neutrons and includes information on the resistance of a number of containing metals to attack by these molten metals. Because of the completeness of the information in the handbook, no effort will be made to cover the field in detail, but a few interesting facts will be mentioned.

Gallium was found to attack the containing equipment more severely than any other liquid metal when conditions were the same. Tungsten showed the best resistance of any metal tried. It was not attacked below 800°C. whereas molybdenum and tantalum were corroded at 600°C. Stainless steels of all types and Inconel were attacked severely at 600°C.

The sodium-potassium alloys were relatively mild in their action on a number of metals although in the presence of oxygen, as from a leak in the system, they attacked vigorously. An interesting summary of the behavior of sodium and sodium-potassium alloys is illustrated in Figure 14. All proportions of these alloys from sodium to potassium appeared to act in about the same way.

In closing this chapter, the authors wish to thank the directors of metal-

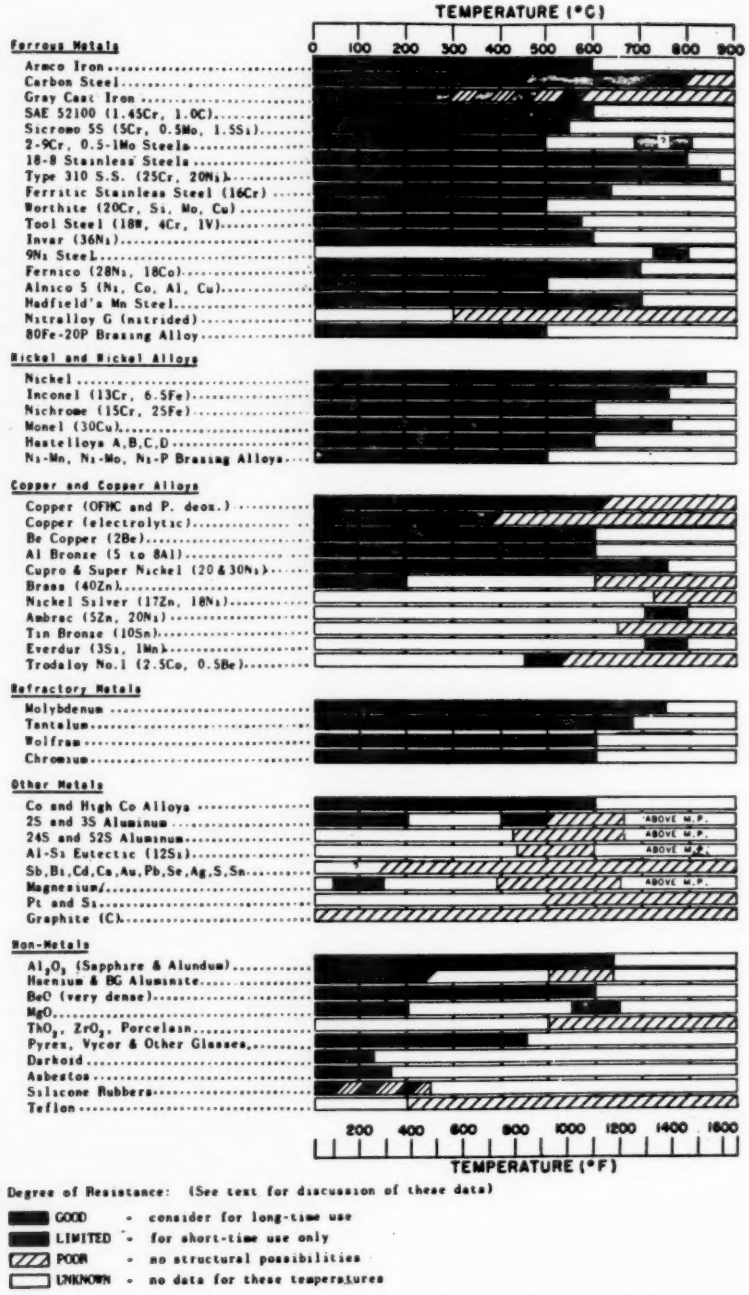

FIG. 14. The resistance of a number of materials to attack by sodium and sodium-potassium alloys.

lurgical activities at other laboratories of the Atomic Energy Commission for calling attention to numerous excellent publications and for contributing unpublished data. Unfortunately, a considerable fraction of the information has had to be omitted because of lack of space. Of approximately 25 valuable papers written by Brewer and his associates only a part were related so closely to the selected fields as to be included in the chapter (15, 20). Contributions from other laboratories have suffered in a like manner. We can only refer the reader to the various scientific indices for the missing material.

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GEOCHEMISTRY[1,2]

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Mineralogy

General.—A new glossary (37) lists 81 mineral species containing uranium or thorium as major constituents and 39 species containing small amounts of uranium or thorium. Many synonyms are also listed.

A study of the fluorescence spectra (40) of a number of uranium minerals showed bands that could be correlated with the presence of uranyl groups or uranate groups. This method may permit proper formulation of some of the complex minerals.

The applications of autoradiography to mineralogical problems have been discussed (65).

Uranium oxides.—X-ray study of the uraninite-thorianite series showed notable variation in behavior of different samples when heated. Metamict pitchblende samples, giving only faint x-ray patterns, were described for the first time. When heated, these give x-ray diffraction patterns either of UO_2 or of U_3O_8 or of a mixture of the two (20). This behavior is correlated with the degree of oxidation before the sample is heated; the highly oxidized samples yield U_3O_8 patterns.

X-ray powder patterns of synthetic solid solutions of UO_2 and ThO_2 (104) showed a systematic variation; the unit cell sizes range from 5.455 Å for pure UO_2 to 5.587 Å for pure ThO_2. The data show a nearly linear relationship between a_o and mol per cent ThO_2. The synthetic solid solutions were heated at 1,200°C. in hydrogen, which may account for divergences from these figures reported for natural uraninites, some of which had a as low as 5.403 Å (5), and for uraninites ignited in air, which had a as low as 5.39 Å (20).

New analyses of uraninite (26, 34, 44, 45, 46, 74), djalmaite (38), samarskite (78), euxenite (74), yttrotantalite (91), and gadolinite (62) are discussed below under Geologic Age Determinations. Scattered through the geologic, mineralogic, and mining literature are many partial analyses, mostly of substances of low U or Th content or of materials not available in economic amounts.

X-ray and optical data (13, 106) indicate the close similarity of the secondary oxides becquerelite and billietite, for which the formulas $PbO \cdot 6UO_3 \cdot 11H_2O$ and $BaO \cdot 6UO_3 \cdot 11H_2O$ have been suggested (13), but, as the x-ray work was not done on analyzed material, it is not yet certain exactly what the relationships are or even whether these are independent minerals.

[1] Publication authorized by the Director, U. S. Geological Survey.

[2] This review is essentially a survey of papers published in 1950.

Minerals of the microlite-pyrochlore group were found to be metamict (5), but gave good patterns after being heated. Comparison of x-ray data showed the dubious mineral djalmaite to be identical with microlite (101, 102).

Euxenite was also metamict but gave an x-ray pattern after heating that could be indexed on the basis of an orthorhombic cell. The specific gravity was increased by heating at 1,000°C., but it decreased slightly on long heating at this temperature. "Tanteuxenite" from western Australia gave a cubic pattern and is apparently not euxenite (5). An analysis of euxenite from Colorado (74) is discussed below under GEOLOGIC AGE.

Two new analyses were published (62) of the complex uranium-bearing niobate-tantalate wiikite, and previous data are reviewed, with discussion of the formula. The status of this highly altered material remains doubtful.

Uranium carbonates, phosphates, sulfates, and other secondary uranium minerals.—Three new carbonates containing uranium were found in very small amounts in Arizona and were described (6). They are andersonite, $Na_2Ca(UO_2)(CO_3)_3 \cdot 6H_2O$; swartzite, $CaMg(UO_2)(CO_3)_3 \cdot 12H_2O$; and bayleyite, $Mg_2(UO_2)(CO_3)_3 \cdot 18H_2O$. Optical and x-ray data are given, and syntheses are described. The same paper gives a new analysis of the complex mineral schroeckingerite and confirms the formula $Ca_3Na(UO_2)(CO_3)_3(SO_4)F \cdot 10H_2O$. Differential thermal analysis curves were published for schroeckingerite, rutherfordine, and liebigite (10). Liebigite was found to be orthorhombic, space group *Bbam* or *Bba;* the unit cell has $a_o = 16.71$, $b_o = 17.55$, $c_o = 13.79$ A, and contains $8[Ca_2U(CO_3)_4 \cdot 10H_2O]$ (29). Optical and crystallographic data on the mineral are also summarized. Uranothallite is identical with liebigite.

Base-exchange studies in the autunite group were continued with the synthesis of the H, Na, and NH_4 members of the uranospinites, $A_2(UO_2)_2(AsO_4)_2 \cdot 8H_2O$ (73). Optical and x-ray data are given. A new analysis of saléeite (72) gave the formula $Mg(UO_2)_2[(P, As)O_4]_2 \cdot 10H_2O$. The mineral is tetragonal, probable space group *I4/mmm;* the unit cell has $a_o = 6.980$, $c_o = 19.813$ A. Analysis of parsonsite from a new locality (35) gave the formula $Pb_2(UO_2)(PO_4)_2 \cdot 2H_2O$; x-ray and optical data are also given. Phosphuranylite (36) was shown to occur at many localities. This supposed uranium phosphate proved to contain calcium, and x-ray powder data showed it to be isostructural with dewindtite, $Pb_3(UO_2)_5(PO_4)_4(OH)_4 \cdot 10H_2O$, but the analyses of the calcium mineral did not correspond closely to that formula. New x-ray and crystallographic data and a new analysis were published (28) for the bismuth uranyl arsenate walpurgite, which is triclinic, with $a_o = 7.13$, $b_o = 10.44$, and $c_o = 5.49$ A, α 101°40′, β 110°49′, γ 88°17′. The exact composition is not yet certainly established.

X-ray study of johannite (47) showed it to be triclinic, pseudomonoclinic, with $a_o = 16.51$, $b_o = 17.98$, and $c_o = 6.83$ kX, α 90°54′, β 90°38′, γ 110°37′. The unit cell contains $Cu_4U_8(SO_4)_8(OH)_{40} \cdot 8H_2O$.

A series of uranyl vanadate compounds of K (=carnotite), NH_4, Tl, Ca (=tyuyamunite), Sr, Ba, Na, Cu, and Zn were synthesized, and x-ray, electron microscope, and base exchange studies were made (75). The data show that the water molecules and the cations occur between uranyl vanadate layers in the crystal structure and that dehydration causes a progressive decrease in interlayer spacing. A new mineral sengierite, $Cu_2(UO_2)(VO_4)O \cdot 10H_2O$, was described from the Belgian Congo (107); it is closely related to carnotite and tyuyamunite. Randite was shown (35) to be a mixture of tyuyamunite and uranotile.

Thorium-bearing minerals.—New analyses of ten monazites (50, 111) were published, with data on the content of the various rare earths for eight of these (111). The radium content of two monazites from Travancore, India, was about 12×10^{-10} gm. per gm. Ra (68). Other analyses are discussed below under GEOLOGIC AGE (38, 62, 74). A new monoclinic thorium silicate, dimorphous with thorite, $ThSiO_4$, was isolated from New Zealand beach sands (50, 81) and named huttonite. It has space group C_{2h}^5, $a_o = 6.80$, $b_o = 6.96$, and $c_o = 5.54$ A, β 104°55′. It is isostructural with monazite, (Ce, La)PO_4, and the discovery raises the interesting question as to the existence of an isomorphous series between the two minerals.

Normal uranothorite as well as a phosphatian variety were also isolated from New Zealand beach sands (50). These were largely isotropic and metamict. X-ray study showed the uranothorite to be tetragonal, space group D_{4h}^{19}-*I4/amd*, with $a_o = 7.12$, and $c_o = 6.32$ A. The structure is that of the zircon type.

Hutton (50) reviews briefly the problems of the metamict state and the origin of microfissures in radioactive minerals.

Thorotungstite, described in 1927 as containing 16 per cent ThO_2, was found to be nonradioactive (9), as the supposed thoria was actually yttria. The name yttrotungstite is suggested.

Analyses of allanite (62, 66, 79, 99, 100) and of weathered allanite were published; they show ThO_2 contents ranging from 0.44 to 4.20 per cent. The ThO_2 content is increased by weathering (62, 100). Uranium is reported in only one analysis (0.13 per cent U_3O_8) but it may not have been looked for in the others. Further data are given below under GEOLOGIC AGE.

A new analysis of sphene (50) showed 0.28 per cent ThO_2. An analysis of gadolinite (62) is discussed under GEOLOGIC AGE. A complete analysis is given (90) of the carbonaceous material called thucolite, from a new locality in Saskatchewan. The analysis gave loss on ignition 94.66 per cent, U_3O_8 0.28 per cent, and PbO 0.32 per cent. A uraniferous opal contained 1.27 per cent U_3O_8.

ECONOMIC GEOLOGY

General.—A review (7) of types of deposits and of production and potential resources by countries furnishes a convenient frame of reference for discussion. Bain classifies the types of uranium deposits as follows:

1. Primary deposits
   (*a*) Pegmatites
   (*b*) High-temperature fissure veins
   (*c*) Mesothermal fissure veins
2. Sedimentary deposits
   (*a*) Bituminous and phosphatic shales
   (*b*) Alluvial or placer deposits
   (*c*) Carnotite-bearing sandstones
3. Oxidized deposits
   (*a*) Precipitated almost *in situ*
   (*b*) Precipitated by an alkaline rock or soil
   (*c*) Precipitated in playa or playa-like deposits

Many occurrences of uranium minerals in pegmatites have been noted, but the total amount of recoverable uranium is small. This conclusion is likewise reached in a more detailed review of the pegmatites (82), which points out that, although a small production of uranium ores may be a by-product of mining feldspar and mica, appreciable tonnages of uranium from such sources have been mined only in Madagascar.

Some high-temperature fissure veins have furnished rich uranium ore, but the deposits have generally been small. The mesothermal vein deposits (Type 1*c*) have been the principal source of uranium. Here are included such deposits as those of Shinkolobwe, Belgian Congo; Great Bear Lake, Canada; and Jáchymov (Joachimsthal), Czechoslovakia. Bain emphasizes the fact that the principal primary deposits have been found around the periphery of massifs or close to the margins of huge shield areas.

Bain's discussion of the sedimentary deposits of Type 2*a* is restricted to the bituminous and phosphatic shales. A more detailed discussion (69) also covers the marine phosphates. These marine shales and phosphorites are of very low grade, containing up to 0.01 to 0.02 per cent U, except for small concentrations (up to 0.5 per cent) in certain organic matter ("kolm") in Swedish shales.

The black shales here considered are high in sulfides and organic matter and contain little or no carbonate; the highest uranium contents are found in relatively thin beds of pre-Mesozoic age. The nature of the uranium-bearing mineral or compound is not known. In contrast, nonmarine black shales as a group are not highly uraniferous.

All marine phosphorites tested so far show concentrations of uranium, as do the phosphatic nodules found in many marine black shales. In general the uranium increases with phosphate content and is thought to be in the phosphate mineral. Like the black shales, the phosphorite beds are characteristically in and are generally associated with unconformities; that is, they were deposited during periods when little else in the way of sediments accumulated.

Uranium in significant concentrations may be found in other types of

marine sediments on further prospecting, but most promising are the sediments rich in organic matter, phosphate, or both, found in relatively thin beds believed to contain all the depositional products of long periods of geologic time. Such beds are most characteristic of those areas where, at the time of deposition, the adjacent land masses were so stable and low that the influx of clastic materials was small; the basin of deposition was large or of such configuration that fine-grained sediments could accumulate, and chemical conditions in the sea water prevented deposition of large amounts of carbonate.

Significant concentrations of uranium in marine sediments other than black shales and phosphorites are known only in beach placer deposits and the gold-bearing conglomerates of the Witwatersrand district of South Africa, whose origin is still disputed.

Placer deposits (Type 2*b* of Bain's classification) will probably not be an important source of uranium, as most uranium minerals seem to be attacked rapidly during the weathering of rocks. These deposits are the source of monazite, (Ce, La)PO_4, the principal ore of thorium. Monazite generally contains 4 to 10 per cent ThO_2 and a few tenths of a per cent of uranium (71).

The "carnotite-bearing sandstones" (Bain's Type 2*c*) are known in several countries, the most important being those of the western United States (33). Uranium is present chiefly as the hydrated potassium and calcium uranyl vanadates, carnotite and tyuyamunite. The uranium-bearing sandstone deposits of the Colorado Plateau ("carnotite deposits") have been the principal domestic source of uranium, radium, and vanadium. The deposits have a spotty areal distribution and are restricted largely to a few stratigraphic zones. Most of the ore bodies are small but range widely in size, and within individual deposits the ore bodies range widely in thickness and grade. The bodies are irregularly tabular or lenticular, with their long axes nearly parallel to the bedding, but the ore does not follow the bedding in detail. The ore minerals mainly impregnate sandstone, but in places fossil plants or bones are richly mineralized.

The ore is thought to have been precipitated from ground water after the enclosing sands had accumulated but before regional deformation. Sedimentary structures that seem to have controlled the movement of these solutions and the features that probably localized the ore deposits are described and their application as guides to ore finding is explained.

The oxidized deposits (Bain's Type 3) are generally small and are of importance only in that they may indicate the presence of a primary ore at depth. Everhart (30) discusses criteria for determining whether deposits of oxidized uranium minerals were derived from uraninite in primary veins.

Two brief summaries of uranium resources of the world also appeared in 1950 (12, 41). A speculative paper (92) attempts to establish a connection between deposits of uranium and thorium and the intersection of mountain chains, especially those of very old orogenies.

Specific deposits—Merritt (70) has summarized exploration for uranium

in the United States, with mention of the Colorado Plateau deposits (see above), and occurrences of primary ore in the Colorado Front Range, in the Coeur d'Alene district (see below), the upper peninsula of Michigan, and at Marysvale, Utah (see below).

In the Coeur d'Alene district, Idaho, uraninite has been found in small amount in two silver mines in quartz-siderite veinlets (103). Associated minerals include pyrite, arsenopyrite, argentian tetrahedrite, and chalcopyrite. At Marysvale, Utah (32, 70, 87), the surface showings were secondary minerals near a quartz monzonite stock, but uraninite has been found at a depth of about 60 ft. Pitchblende was found in deep levels of a silver mine in Colorado (89). No radioactivity anomalies were apparent at the surface, and the host rock—a quartz monzonite—showed normal radioactivity. The carnotite deposits of the Colorado Plateau are described in two papers (33, 58), and a small occurrence of carnotite was noted in Missouri (76, 77). Here the uranium was apparently leached from a shale and redeposited in limestone below.

Two summary accounts (52, 60) of Canadian uranium deposits give lists of all deposits and brief accounts of the largest, including those at Great Bear Lake, which is one of the two largest in the world. Exploration has been particularly active in the Goldfields (or Beaverlodge Lake) district, Saskatchewan, where dozens of prospects have been located (3, 17). Uraninite occurs with hematite and carbonates in veins and stringers in fractures. The paragenesis is complex (19), and the mineral assemblage includes a large number of sulfides and, in places, selenides (90). Similar, apparently smaller deposits have been found in the Northwest Territories (43) and in the area north of Lake Superior near Theano Point (56). A few occurrences of uranium minerals have been noted in British Columbia (97).

Only a few small occurrences of radioactive minerals are known in Turkey, and prospects for discoveries there appear to be poor (8).

Methods of prospecting and concentration.—Instruments for prospecting for uranium are discussed in two papers (14, 27). Scintillation counters have become important in such work. Keevil (55) has reviewed the applications of radioactivity measurements to problems of economic geology and has given data showing the radioactivities of ore and gangue rock from several mining districts.

Three papers deal with methods of concentration of uranium ores (15, 54, 95), including the use of an electronic device actuated by a Geiger-Muller tube. Church (18) has shown that with proper chemical treatment, certain nonradioactive minerals, such as galena and apatite, can assume a radioactive surface film and can then be concentrated by such electronic methods.

Abundance and Distribution of Radioactive Elements

General.—A review summarized modern theories of physics on the origin of the observed abundance and distribution of the elements (4).

The occurrence, abundance, and distribution of the radioactive elements have been reviewed (31, 88). Both uranium and thorium are concentrated in acidic igneous rocks in which their content is three to six times that in basaltic rocks. The ratio of thorium to uranium averages 3 to 4 for igneous rocks. However, the ocean contains much more uranium than thorium. This is probably largely because of the fact that monazite and zircon, which contain most of the thorium of igneous rocks, are highly resistant to weathering. It may be in part a result of selective adsorption and precipitation of thorium, but marine sediments have much lower thorium-uranium ratios than igneous rocks.

Radioactive elements in rocks.—Earlier measurements of the radium content of ultramafic igneous racks are discussed (24). Much of the radioactive material in these rocks was introduced during late-stage alteration. Study of 12 meteorites (23) showed very low radioactivity. If the core of the earth is similar to this material, radioactivity could not be an important source of heat in the core. Preliminary data obtained by alpha-counts are given for a series of samples of Columbia River basalts (48), which show higher activities than most basic igneous rocks. Other measurements (94) are discussed below. Measurements by gamma-ray logging (22) of rhyolite porphyry in Missouri indicate that the radioactivity is largely due to potassium Three granites from India, studied by the emanation electroscope, contained 1.6 to 2.6 $\times 10^{-12}$ gm. per gm. Ra (68).

The study of radioactivity of rocks by the use of photographic emulsions continued. Details of methods were published (86), including methods for the quantitative estimation by alpha-track counts of the content of radioactive elements. A brief note (85) gives results on a granite from the Vosges Mountains. A detailed study of granitic rocks, gneisses, and mica schists (21) shows extreme variation both in the distribution of radioactive material and in its nature. Some radioactive inclusions were high in uranium (up to 70 per cent), others were high in thorium. The method was also applied (42) to rocks containing small amounts of thorium.

Data on the radioactivity of deep-sea sediments have been summarized briefly (110). Radium determinations were made (84) by the emanation method on three cores from the Tyrrhenian Sea, and possible modes of origin are discussed. Measurements by alpha-counting were given for samples from the Gulf of Mexico (48). New determinations were published (59) of the thorium content of seven shales, which contained 0.6 to 1.9 gm. per ton of thorium, whereas their uranium content was 10 to 200 gm. per ton.

Radioactivity of waters.—A review (51) gives a tabulation of the radon contents of strongly radioactive springs, and discusses the seasonal variation, relation to rate of flow, and the radon content of the gases in the hot springs. Radioactivity measurements of 10 springs in Lebanon and Syria showed activities ranging from 0.007 to 6.15 millimicrocuries per liter (25). Data are given for 17 waters from Travancore, India (68). Thorium was determined by the thoron method in Japanese springs (93). The radioactivity of Hun-

garian waters is discussed (98); it is attributed to the leaching of deep-seated granites.

Geothermal significance.—The heat flow within the earth and its effect on the earth's thermal history have been computed (105) for several models of the earth, assuming constant temperature at the surface and heat loss from the interior by conduction only. Another paper (63) is particularly concerned with the energy contributed by radioactive decay. Calculations (108) based on new data for the decay of K^{40} show this to be a more important contributor of energy to the earth's crust than hitherto supposed. New measurements by alpha-counting (94) of the radioactivity of rocks around the Round Lake Ontario, batholith, indicate a migration of radioactive elements toward the top of the batholith. Detailed new measurements (11) were made of thermal conductivity of rocks from the new Adams Tunnel in the Rocky Mountains and of temperature gradients in the rocks of the tunnel. The data, chiefly on granitic rocks, indicate and approximately uniform distribution of radioactivity throughout the "granitic" layer of the earth's crust.

Geologic Age Determinations

General.—Progress during the period April, 1949 to April 1950 is summarized in the valuable Annual Report of the Committee on the Measurement of Geologic Time (67). Some unpublished data are included; these are mentioned below. There is also included an annotated bibliography with critical comments. An approximated geologic time scale is given.

Calculations, based on data for abundance and half lives, are given for maximum and minimum time limits of formation of the elements, assuming them to have been formed simultaneously (64). The best figure for the maximum is 4,600 million years, based on data for uranium.

Lead-uranium-thorium ratios.—Analyses for U, Th, and Pb were made (46) on uraninite and monazite from the post-Delhi pegmatites of Rajputana, and isotopic analyses of the lead (7.95 per cent) in the uraninite were made with the mass spectrometer. This gave for the relative proportions Pb^{204} <0.001, Pb^{206} 100.00, Pb^{207} 6.39, Pb^{208} 0.806. Closely agreeing apparent ages of 740, 733, and 733 million years for the uraninite were derived from the ratios AcD/RaG, RaG/U, and AcD/U, respectively; that derived from the ThD/Th ratio was 935 million years, presumably indicating loss of thorium.

Analysis of uraninite from the Gaya India, district, gave Pb 8.92, U64.3, and Th 8.12 per cent (44). Isotopic analyses of the lead gave the relative values Pb^{204} <1/20,000, Pb^{206} 100.00, Pb^{207} 7.20, and Pb^{208} 4.68. Ages in millions of years were calculated as 995, 883, 912, and 1,003 from the ratios AcD/RaG, RaG/U, AcD/U, ThD/Th, respectively. Causes of these divergences are discussed. The best age is stated as 955 ± 40 million years.

A complete analysis of allanite from Bahea, India, was published (79). From the determinations (ThO_2 0.53 per cent, U_3O_8 none, PbO 0.02 per cent), the age is calculated to be 830 million years. No isotopic analyses were made. A complete analysis (78) of samarskite from Nellore gave UO_2 6.93 per cent,

ThO_2 1.21 per cent, and PbO 2.04 per cent. Isotopic analysis of the lead will be made later. Uraninite from Gordonia, South Africa (45), on which widely divergent results have previously been reported, was analyzed. A sample contained Pb 10.21 per cent, U 55.00 per cent, and Th 11.75 per cent. Isotopic analysis of the lead gave the relative vaules $Pb^{204} < 1/20{,}000$, Pb^{206} 100.00, Pb^{207} 7.35, and Pb^{208} 5.42. This gives ages (in millions of years) as 1,037, 1,148, 1,106, and 914 from the AcD/RaG, RaG/U, AcD/U, and ThD/Th ratios, respectively. The most probable age is considered to be $1{,}025 \pm 10$ million years.

A complete analysis was reported (66) of allanite from a pegmatitic lens in the Monson granodiorite near Greenwich, Mass. The averages of several determinations were Pb 0.032 per cent, Th 1.530 per cent, and U 0.095 per cent, which correspond to an age of about 390 million years. Isotopic analysis has not yet been made.

Analyses are given (74) of two uraninites from Colorado, of monazite from New Mexico, and of monazite from Manitoba for which isotopic analyses had previously been published. A complete analysis is also given of euxenite from Trout Creek Pass, Colorado, which contained U 3.41 per cent, Th 4.25 per cent, and Pb 0.293 per cent. Partial analyses of two pitchblendes from Saskatchewan (26) gave ages of 583 and 764 million years, but the samples were altered, so that the results are inconclusive.

Four analyses of uraninite from the states of Paraiba, Rio Grande do Norte, and Minas Gerais, Brazil, were published (34). No thorium was reported, and isotopic analyses have not been made. The analyses all give ages of 500 to 520 million years.

Partial analyses of ten Brazilian monazites (39),[3] both eluvial and pegmatitic, gave ages of 360 to 410 million years for five, and ages of 1,150 to 1,220 million years for five others. No uranium is reported in any of these, and no isotopic analyses have been made. It is believed by these authors that monazite is better in general for age determinations than uranium minerals, which are more subject to alteration. Three analyses of djalmaite from Minas Gerais show considerable increase of PbO and decrease in U content with weathering.

A complete analysis (91) of yttrotantalite from Bjortjenn, Norway, gave U_3O_8 5.6 per cent, ThO_2 1.8 per cent and PbO 0.5 per cent, leading to a calculated age of 661 million years.

Complete analyses were published (62) of gadolinite and two samples of allanite, and two partial analyses of monazite were also reported. The samples were from Finland, northern Lapland, and the Karelian S.S.R. Uranium is not reported, and no isotopic analyses have been made. All five samples give calculated ages in the range 1,114 to 1,192 million years.

A method was described (61) by which age determinations can be made on small amounts of accessory minerals, such as zircon, by spectrographic

[3] The analyses, with discussion, are given by Marble (67, pp. 47–51).

analyses for lead and alpha-count determinations of radioactivity. This method may permit age determinations on many rocks to which no other method is now applicable, and it is believed that the analytical errors may not exceed 10 per cent.

Helium.—A new study (49) showed that treatment of crushed granites with dilute hydrocholoric acid leached appreciable amounts of uranium and thorium from the rocks, whereas diabase and rocks from deep cores showed less loss. Ages determined by the helium method on samples that had been acid-leached were in much better agreement than those made on untreated rock. It is possible therefore that discordant age determinations, previously attributed to loss of helium by migration, were actually in error because of surface enrichment of the samples by radioactive elements. Further study is obviously needed.

Data on "excess helium" in beryl and other minerals (16) show low helium contents for minerals not having close-packed structures. Another paper (57) shows that inclusions of rutile, cassiterite, and garnet in beryl contain much more helium than the beryl itself and give geological ages nearer the truth. Isotopic determinations are needed for accurate age determinations.

Strontium-rubidium.—A detailed review of the possibilities of age determinations by measurements of the strontium-rubidium ratio appeared in 1949 (1). The method has been shown to be useful for pegmatite minerals. Further improvements have been made (2) and the extension of the method to biotite is possible; this would greatly extend its usefulness.

Argon-potassium.—The radioactivity of potassium and the use of A^{40} determinations are discussed by Jeffreys (53). There is still some uncertainty as to the decay constants, but the most recent determinations (96) are in good agreement with the best earlier work. The method gave (83, 94a) 20 million years for the age of the potassium deposits at Buggingen, Germany.

Carbon and nitrogen.—No further age determinations by the C^{14} method were published in 1950, but several laboratories are working on the method.

The isotopic abundance of N^{15} in the nitrogen occluded in radioactive minerals such as uraninite and samarskite was shown (109) to vary with the geological age. The cause of this variation is not clear, but further work may show this to be useful in geologic age studies.

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GENETIC EFFECTS OF RADIATION[1]

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Two major features mark the literature of radiation genetics for the year 1950. Several important papers of a theoretical nature have been published on the genetic consequences of irradiation for man. There have been a number of findings which tend to make the hit theory, at least in its simpler form, less plausible than it formerly was. Reviews of the literature which may be mentioned are Muller's Sigma Xi lecture (1), the chapter by Fano, Caspari & Demerec (2) in Glasser's *Medical Physics*, portions of the chapters by Catcheside (3) and by Edelman (4) in the *Annual Review of Physiology* and a review by Forssberg (5). A symposium on radiation genetics (6) sponsored by the Biology Division of Oak Ridge National Laboratory was published.

Genetic consequences for man.—The discussion of the genetic consequences, for man, of exposure to radiation has produced theoretical papers by Evans (7), Muller (1, 8, 9, 10), and Wright (11). Brief evaluations are also given in a number of publications (12). The estimates of the potential hazard of the increased exposure to radiation which results from present-day medical practices and the increasing use of radioactive materials have ranged from Evans' claim (7) that the hazard is of little importance to Muller's judgment (1, 10) that it is of major importance. The differences in opinion result partly from the fact that basic quantitative data are not yet available for man, partly from the great complexity of the situation, and partly from the fact that agreement on the basis for evaluating the importance of the damage has not been reached.

Evans (7), accepting certain figures from the literature and emphasizing completely recessive genes, makes calculations that would lead one to believe that a total dose of 250 r would, on the average, lead to only a 1.5 per cent increase in "showing" of the mutant genes. The calculations are based on certain assumed values for spontaneous and induced mutation. Wright (11) has shown that a value for the spontaneous rate, which he regards as more probable than that given by Evans, might change such calculations by a factor of 100. Moreover, both Wright (11) and Muller (1, 8, 9, 10) have emphasized that most mutations are probably not strictly recessive, although in usual laboratory procedure they can be treated as such. From the point of view of the effect on populations of an increased mutation rate, even a very small degree of dominance is important. Thus Muller (10) points out that genes with as little as 2 per cent dominance would still exert the major part of their damage in the heterozygous rather than the homozygous condition. Evans (7) recognizes that the effect of dominant mutations would be

[1] This review is essentially a survey of papers published in 1950.

[2] Under Contract W-7405-eng-26 for the U. S. Atomic Energy Commission.

relatively larger, but apparently considers only dominants with major action. Muller (1, 8, 9, 10) has emphasized that by far the most frequently arising mutants are those with very small effects. Such mutants, because they are not strongly eliminated by selection, accumulate in the population and spread their slight, but nonetheless damaging influence over many individuals. Thus, the total damage which one such mutation causes, though less concentrated in time, is probably as great if not greater than the much more readily detectable mutant genes with major action.

The question of what criterion to use in judging the harmful effect of radiation has not been settled, much less the quantitative change in the criterion which can be considered acceptable. Evans (7) uses the ratio of the "showing" of mutations in the irradiated as compared to the "unirradiated" population. Wright (11) recognizes that a number of criteria are possible but chooses the reproductive value of the population for most of his calculations since it is more readily evaluated quantitatively. He discusses briefly the case in which the reproductive value remains unchanged although the genetic quality of the population is altered. Muller (1, 10) discusses both the increase in showing of mutations per generation and the total amount of damage spread over many generations.

Wright (11) calculates the effects upon reproductive rate for completely recessive genes and for partial dominants. In both cases, the final equilibrium value is independent of the selective disadvantage of the mutants and is dependent only upon the rates of mutation. Wright (11) develops certain special cases in which the reproductive rate of the mutant type remains the same relative to normal but, as the mutant type increases, the reproductive rate of the population as a whole decreases. Under such circumstances, the reproductive rate of the population may fall to zero; i.e., the population collapses. Under other circumstances, the reproductive rate of the population may remain constant although the genetic quality changes. No doubt many such special situations might be set up. This emphasizes that we are dealing with population equilibrium situations, and so the effects of percentagewise small changes in population constants may have disproportionately large effects as a result of upset in the equilibrium.

Wright (11) concludes that the great gaps in our knowledge make it impossible to take any judgment of genetic consequences in man very seriously. He believes that there is a strong possibility that cumulative doses of about 300 r may have important effects upon the offspring and descendants of those exposed, while 30-r exposures may not be negligible. He does not believe that there is much threat to the persistence of the population from this cause.

Muller (10) believes that, because of the relaxation of selection which has been occurring in recent times, the mutation rate may be near the critical point for maintenance of the population and that whether a new equilibrium can be established in the future might depend upon relatively slight changes in the mutation rate. Obviously the questions involved here are very difficult

ones involving much information about the nature of human populations and the selective processes going on within them in addition to more precise estimates of both spontaneous and induced rates of mutations than are now available. The calculations which have been made make it obvious that it is not possible to reach agreement upon the magnitude of the increase in "showing" of mutant effects, much less upon the more difficult problem of whether a given effect will be likely to be disastrous to the population. When one adds the moral problems of possible damage to individuals in future generations, even though the population as a whole is maintained [see Muller (9)], it can be appreciated that the problem is indeed one of great complexity and that hasty judgments ought to be avoided.

For evaluating effects upon populations, much of the basic information upon kinds of mutations, frequencies with which they occur, role of chromosomal aberrations, etc., is derived from work with *Drosophila* and is excellently reviewed in two of Muller's papers (1, 8). One need is a measure of the rate of induction of mutation by radiation in some organism more nearly related to man than is *Drosophila*. For this purpose, the mouse is the obvious choice. Charles (13) reviews the small amount of previous work and gives his own results founded upon the analysis of 3,072 sperm. Three classes of mutants are distinguished: dominants, sex-linked lethals, and chromosome translocations expressing themselves as semisteriles. He finds that new mutations of all kinds arise in about 1 per cent of sperm cells per 100 r. He concludes that approximately 50 r double the mutation rate. It must, of course, be remembered that this rate is for detectable mutations which, as Muller has shown for *Drosophila*, are expected to be much less frequent than those which cannot be detected by simple methods of examination. Charles' results are for repeated exposures to small doses. Others using large single doses have found a very much higher value for translocations. Recently this higher value has been confirmed for mice by Russell (15). A number of other quantities besides mutation rate will be needed to make accurate estimates of the genetic hazard for man. Of papers valuable in this respect and dealing directly with radiation may be mentioned the estimate for *Drosophila* of the number of X-chromosome loci by Herskowitz (16), and of the number of second chromosome loci by Wallace (17), and the estimates of viability of spontaneous and x-ray-induced mutations in barley by Gustafson & Nybom (18).

Experimental alteration of sensitivity and the mechanism of action.—Much interest has been aroused in recent years in the finding that various agents can modify radiosensitivity in respect to mutations and chromosome aberrations. One would not expect that the primary photochemical absorption of the quantum of energy would be influenced by temperature, oxygen tension, and other similar factors. On the hit theory, at least in its more usual form, this primary absorption leads directly without intermediate reactions to the alteration in the gene or chromosome which is recognized as a mutation or chromosome break. Thus the frequency with which mutations or

breaks are induced should not be influenced by such agents. A complication enters into the interpretation of actual experiments, for the detection of broken chromosomes depends upon the broken ends joining in new arrangements and not rejoining in the old arrangement (restitution). There is every reason to expect this latter process to be affected by external influences. Moreover, the fact that many so-called mutations can be shown on careful study to be due to position effect or to small deficiencies [Muller (1, 8); Lewis (19)] renders it difficult or impossible to exclude the effects of the recombination of broken ends from studies of gene mutation. Nevertheless, investigations over the years have seemed to show that gene mutations were more or less independent of external agents, and it appeared to be possible to explain such effects as the influence of oxygen on chromosome aberration production as shown by Thoday & Reed (20) as effects on the recombination mechanism. This has become much more difficult as a result of recent work on oxygen, temperature, and light. One is led to admit as a strong possibility that the production of mutations and chromosome breaks is itself influenced by environmental agents with the corollary that such breaks and mutations must, at least in part, be produced by processes secondary to the primary absorption of energy.

Riley & Giles (21, 22) have continued their studies of the effect of oxygen on the production of chromosome aberration by x-irradiation of *Tradescantia*. They found that the oxygen tension during irradiation is critical and that oxygen tension after irradiation has little, if any, effect. Since the recombination of broken ends continues for some minutes, they take this as strong, though perhaps not final, evidence that it is the breakage mechanism which is affected. They suggest that the effect may be by way of peroxide or some other substance produced by irradiation. Giles & Riley (22) and Giles & Beatty (23) were able to demonstrate conclusively that the oxygen tension rather than the presence of other gases or pressure changes is the determining factor.

Baker & Sgourakis (24) have demonstrated a similar effect of oxygen tension upon the induction by x-rays of lethal sex-linked mutations in *Drosophila*. Such mutations are in part associated with detectable chromosome changes but in part are not [see Muller (8)]. Baker & Sgourakis (24) also demonstrated that flies irradiated in oxygen at 2°C. are more affected than are flies irradiated at 26°C. On the other hand, temperature has no effect when the irradiation is carried out in nitrogen. They suggest that the temperature relations are due to the greater solubility of oxygen at low temperature.

Fabergé (25, 26) has carried out combined studies of temperature and oxygen tension with *Tradescantia* pollen. A wide range of temperatures down to −192°C. was used; the curve for the effect very closely parallels that for the production of hydrogen peroxide. Some breaks still occur at −192°C., although no peroxide is produced, suggesting that there may be some breaks produced by a direct absorption of quanta. Giles & Riley (22)

likewise found some breaks in the complete or nearly complete absence of oxygen suggesting that some breaks may be produced directly.

On the other hand, Hewitt & Read (27) have been unable to demonstrate an effect of oxygen upon *E. coli* phage irradiated in broth. They believe that the hit theory is adequate to account for their results.

The evidence that mutations may be produced by indirect mechanisms is still better for ultraviolet. Stone and his co-workers have continued their work which has demonstrated that mutations in bacteria and fungi can be induced by ultraviolet-irradiated media. Wyss *et al.* (28) and Haas *et al.* (29) have reviewed the work which has shown that mutagenic substances are produced in broth irradiated with ultraviolet or treated with hydrogen peroxide. Such action has been shown for several species of bacteria. Wagner *et al.* (30) have demonstrated the same thing for the mold *Neurospora* in which a more detailed genetic analysis is possible, leaving no doubt that gene mutations are involved. Thus, peroxide and ultraviolet are able to produce mutagenic agents and so mutations indirectly. Ross (31) suggests that nitrogen mustards, radiation, and peroxides can act through "electrophilic centres" to produce mutations. Clark *et al.* (32) have shown that irradiation of medium or treatment of it with hydrogen peroxide increases the frequency of gene recombination in *E. coli*. They suggest that some apparent mutations in bacteria may be the result of uncovering of recessives in diploids by recombination.

Further evidence that genetic changes induced by ultraviolet may be brought about indirectly rather than by direct absorption of quanta is given by the phenomenon of photoreactivation. The early work on this subject is reviewed by Kelner (33). Briefly, if the organism is exposed to ultraviolet (usually 2537 Å) and then to very long ultraviolet or to short visible of high intensity (approximately 3000 to 5000 Å) less effect is produced than if it is exposed to ultraviolet and then kept in the dark. Since the photoreactivating light can be given within a period of some time (half an hour at least) after the ultraviolet and still have an effect, it is obvious that some sort of indirect action is involved. Novick & Szilard (34) Kelner (33), and Newcombe (35) demonstrated the effect for mutation in the bacterium *E. coli*. Goodgal (36) has found it for mutations in *Neurospora*, and Kimball & Gaither (37) for changes believed to be mutations in *Paramecium aurelia*. Dulbecco (38) has demonstrated it for inactivation of bacteriophage. Photoreactivation has also been found for a variety of nongenetic effects, such as cleavage delay in sea urchin eggs [Blum *et al.* (39); Marshak (40)], delay in cell division, and other effects in *Paramecium* [Kimball & Gaither (37)], which indicates that it is a general feature of ultraviolet damage to the cell. Apparently the effects of ionizing radiation are much more stable to photoreactivation than are those of ultraviolet [Blum *et al.* (39); Dulbecco (38); Kimball & Gaither (37); Newcombe (35)]. Haas *et al.* (29) have demonstrated photoreactivation of the ultraviolet effect in producing mutagens in broth. This result, together with the theoretical formulations of Novick & Szilard (34) and Dulbecco (38)

make it probable that some substance is produced by the ultraviolet which is subject to photoreactivation and can lead to such diverse consequences as mutation and delay in cell division. However, it appears that a proportion of the ultraviolet effect is not subject to photoreactivation and may possibly represent a more direct action of the radiation.

Infrared is known to increase the frequency of chromosome aberrations [see Sax (14)]. Yost (41) has recently found that posttreatment of *Tradescantia* microspores with infrared as long as 96 hr. after x-irradiation increases the frequency of aberrations. The studies suggested a nonlinear relation to infrared dose. Glass (42) found an increase of both chromosome aberrations and sex-linked lethals following either pre- or posttreatment of *Drosophila* males with infrared. This contrasts with the findings of Kaufmann [see discussion following Sax (14)] that posttreatment of *Drosophila* was without effect. The mechanism of the infrared effect is not really understood as yet. However, it is conceivable that it is upon the recombination process.

An effect of heat upon ultraviolet-treated bacteria has been reported by Stein & Meutzner (43) .They found that the survival of *E. coli* which had been exposed to ultraviolet and then exposed to high temperature was greater than it was when more usual temperatures were used.

Sommermeyer (44) believes that the inactivation of phage by radiation involves a spread over the whole particle, whereas mutation is more localized. Mazia & Blumenthal (45) investigated the inactivation of enzyme-substrate films by x-rays. They find such films are inactivated by quite low doses, and they propose the hypothesis that there is a spreading of the effect of ionization.

Cohen & Arbogast (107) present evidence that the synthesis of desoxyribonucleic acid (DNA), but not purines and pyrimidines, was inhibited in phage by ultraviolet under conditions in which mutual reactivation occurred and that DNA was not synthesized until intact phage was formed. Thus they believe that the effect of ultraviolet is upon the DNA. Giese (108) has reviewed the action of ultraviolet upon the constituents of protoplasm and considers effects both upon the proteins and the nucleic acids.

Despite the fact that the evidence from the oxygen effect suggests that chromosomal aberrations and gene mutations may be produced less directly than the hit theory would have suggested, it is not surprising that Whiting (46) has been unable to demonstrate an effect of irradiated cytoplasm upon mutation in a nucleus introduced after irradiation. She irradiated females of the wasp, *Habrobracon*, and mated them with males having marker genes. A certain number of haploid male offspring were produced which derived their nuclei from the sperm, the egg nucleus having been killed by the irradiation. These androgenetic males showed no increase in mutation rate even at doses high enough to cause a failure of most eggs to develop, presumably as a result of cytoplasmic injury. Since a considerable time had to elapse between irradiation and the introduction into the egg cytoplasm of the male pronucleus, an increased mutation rate would have been found only

if a more or less stable mutagenic substance had been formed in the cytoplasm. The experiments demonstrate that this was not the case.

One of the pieces of evidence for the hit theory has been the fact that mutations follow an exponential law of increase with dose. This has usually been taken to mean that each mutation arises as a result of a single event independent of any other events. Opatkowski (47) and Opatkowski & Christiansen (48) believe that an equally good fit to the available data can be obtained if one assumes that each mutation is the result of many random events. Opatkowski (47) says

> It is not the intention of this note to prove or disprove this or other theories in radiogenetics, but to point out only that the apparent linearity of the frequency-dose curve should not be considered as a proof of the single event theory.

No doubt a number of other relations could also be made to fit the data as Opatkowski & Christiansen (48) point out. The evidence for the hit theory has never rested upon the exponential relation to dose alone but has used this in conjunction with other evidence, such as the independence of the time-intensity factor. Thus it seems doubtful whether the fact that other relations can be made to fit the data is very disturbing to the theory unless it can be shown that these other relations can account for all the facts. However, this work does warn against too facile generalization from form of curves.

Three general articles which especially concern the mechanism of the action of radiation are those by Fano *et al.* (2), Forssberg (5), and Reitz & Longmire (49). Fano *et al.* (2) review both the hit theory and the indirect action theory. They point out that the difference between the two is not really great when a restricted form of the hit theory is used. Forssberg (5) points out in particular some of the difficulties with the hit theory. Taken altogether, the hit theory has had serious doubts cast upon it, at least in its more extreme forms. It seems established that mutational changes can be brought about through indirect effects of radiation, though it is certainly possible, perhaps even probable, that direct ionization of gene and chromosome molecules are also involved. In any case, much of the formulation of the theory which depends upon the localization of the effect will probably remain useful and valid.

Differences in sensitivity due to biological factors.—Differences between cells in their sensitivity to radiation have long been known. A number of pieces of work have appeared during the year which add information to the subject. Differences between strains and species are well known from previous work. Polson & Dent (50) report that antigenically different strains of African horse-sickness virus show different rates of inactivation with ultraviolet. Clark & Kelly (51) have shown for *Habrobracon* prepupae and pupae that diploid males and females are more resistant to radiation than are haploid males, as one might expect if mutational changes in somatic cells can lead to death and abnormal development. In the haploid, but not in the diploid, recessive changes would have an effect.

Muller and co-workers (52) have compared the production of mutations in the oöcytes and oögonia of *Drosophila.* The oöcytes with their condensed chromosomes show approximately the same rate of mutation induction and production of deficiencies as do the spermatozoa, whereas the oögonia with their attenuated chromosomes show considerably lower effects. However in both, unlike spermatozoa, gross rearrangements were not found, which suggests that recombination must occur fairly promptly. Crouse (53) has found similar evidence for *Sciara coprophila* that reciprocal translocations are not produced in eggs but are in sperm. She suggests that nonhomologous chromosomes must fail to contact one another before union of broken ends. These two pieces of work make it clear that differences in factors influencing union of broken ends of chromosomes may strongly influence the sensitivity.

LeFevre (54) has studied somatic mutation of specific genes in *Drosophila* as induced by x-rays. He finds rates for somatic cells which are quite similar to those for germ cells and concludes that the rate of mutation is independent of the kind of cell.

There have been three studies of the relation of chromosome aberration production to stage in the mitotic cycle during which irradiation was performed. Sparrow *et al.* (55) using *Trillium erectum* found the greatest sensitivity during the late prophase and metaphase of the first meiotic division and the least during early postmeiotic interphase. Attempts to establish a correlation with the pentosenucleic acid and DNA content were unsuccessful. Sparrow & Maldawer (56) report that changes in sensitivity in *Trillium* can be related both to the frequency of breaks and to the rejoining process. Bishop (57) working with *Tradescantia,* found the highest sensitivity during late prophase and metaphase-anaphase. He suggests that spiralization and the spindle lead to stresses which cause the broken ends to separate and that they are then held apart by the matrix.

Chronic irradiation.—With one-hit aberrations and gene mutations, it has been found that the same effect is produced by the same total dose whether it is given in a short or long period of time [see Muller (1, 8)]. However, with two-hit aberrations, there is clear-cut evidence for an effect of the intensity factor [see Sax (14)]. When the dose is spread over many cell generations, still another factor enters into the results. There may be selective elimination of cells with aberrations or mutations so that the apparent frequency is less than would be expected. Sax (58) has exposed *Tradescantia* to 1.7 r of γ-rays per day for varying periods. He found after 22 weeks (262 r) that there were 0.5 per cent breaks, whereas the same dose would have produced 30 per cent if given in a few minutes time. The number of breaks increased up to three weeks of irradiation and then leveled off. When irradiation ceased, about three weeks were required for return to the normal level. This suggests that cells with aberrations either stop growing or are outgrown. Sax points out that the differences in the nature of the growth processes of plants and animals make it doubtful whether these findings could be applied to the latter, and thus it might be expected that animals would be more vul-

nerable to radiation. It is obvious how important this finding would be if such selective elimination of genetically damaged cells occurs in all dividing tissue.

Sparrow (59) has also investigated the results of exposing *Tradescantia* to chronic irradiation. He found that the plants showed little or no growth if exposed to as great an intensity as 30 r per day. However 7.5 r per day had little if any effect on growth. A significant increase in the number of micronuclei (acentric chromosome fragments) was found for exposures to 84 mr per day for 32 days.

Wallace (60) reports that exposure of developing *Drosophila* to 108 r per day for varying numbers of days led to a linear increase in recoverable lethals up to 20 days exposure, but the percentage of lethals at 25 days exposure was the same as at 20 days. No explanation for this finding is offered. One can wonder whether some sort of equilibrium between production and elimination such as Sax found in *Tradescantia* may have been involved.

However, it may be recalled that Charles (13) found with chronic exposures of mice that, while many fewer translocations were produced than would have been expected from a single exposure, the rate for dominant visible mutations was about the same as had been found in previous experiments with single acute exposures. Thus there is no evidence in this work for elimination of mutations over the course of many weeks irradiation.

Comparative effects of various radiations.—Quastler (61) and Regehr *et al.* (62) have compared the effectiveness of x-rays from a 20-M.e.v. betatron with x-rays from an ordinary therapy machine. Among other things, sex-linked lethals of *Drosophila* were studied. Both investigators found that the high energy radiation was about 60 per cent as effective as the low when measurements were made with Victoreen chambers. Regehr *et al.* (62) believe this shows that at least part of the lethals require more than one ionization for their production.

Dieckmann *et al.* (63) found that 3-M.e.v. electrons were more effective than 180-kv. x-rays in inactivating *E. coli.* Both curves were essentially linear on a plot of log survival against dose. They point out that the result is that expected if killing were due to a single ionization. Paul & Schubert (64) and Schermund *et al.* (65) have compared the effects of high energy electrons and x-rays upon barley. Schermund *et al.* (65) found that the frequency of chromosome fragments was less with 4-M.e.v. electrons than with x-rays (hvl 0.25 mm. Cu). This is to be expected if more than one ionization is required for breakage as had been found previously [Giles & Conger (68)]. Paul & Schubert (64) found that length of leaves and chromosome breakage were both more affected by x-rays than by 6 M.e.v. electrons. They also believe that certain qualitative features of the reactions of length of leaf to radiation may not be the same in the two cases.

Conger & Giles (66) and Conger (67) have reported upon the effect of slow neutrons from the Oak Ridge pile on chromosome breakage in *Tradescantia.* They found that 99 per cent of the effect of thermal neutrons could

be accounted for by reactions with hydrogen, nitrogen, and boron, 77 per cent by the last two. The reaction with nitrogen results in the emission of a proton, while an alpha particle is emitted from the boron reaction. The surprisingly important role of the trace element boron is the result of its high capture cross section combined with the fact that it produces a heavily ionizing alpha particle which loses all its energy within the tissue. That the major effect was due to protons and α-particles was confirmed by the essentially linear increase in exchanges involving more than one break. Such exchanges have previously been found to increase linearly with dose in the case of heavy particles but to increase as a power of the dose greater than one with x- and γ-rays. The important effect of boron was further confirmed by Conger's finding (67) that boron-enriched plants were more affected than those which were not enriched. Conger & Giles (66) report that thermal neutrons were about 11 times as effective as x-rays when measured in terms of r.e.p.

Giles & Conger (68) found that chromosome interchanges show a linear relation to fast neutron dose. The less energetic the neutrons the more efficient they were in inducing the interchanges. This is in line with the evidence that several ionizations are required to produce a chromosome break, for the greater density of ionization along the track of a slower particle would be more efficient.

Englehard & Houtermans (69) compared α-particles and ultraviolet in the inactivation of *E. coli*. In both cases, they found that the early part of the curve showed essentially an exponential relation with dose but deviated at higher doses. They believe that this can be explained as a combination of a one- and a many-hit curve. The formal calculations lead, for the many-hit part, to a five-hit curve for α-particles and a 50-hit curve for ultraviolet. It certainly seems quite possible that killing of bacteria could be due to more than one process, whether or not the somewhat formalized application of the hit theory which is used in this paper is appropriate.

A number of papers have appeared in which a variety of ionizing radiations have been investigated for genetic effects. Randolph (70) investigated maize and Brown (71) cotton which had been exposed to an atomic bomb explosion at Bikini. Both found evidence of chromosome aberrations. Randolph (70) reports that chromosome aberrations were observed with approximately the same frequency as in x-irradiated material. With both radiations, there were many more translocations than other types of aberrations. Frolik & Morris (72, 73) report the production of mutations in maize pollen exposed in the Argonne heavy water pile. Diller and associates (74) report the production of mutations in *Aspergillus niger* by soft x-rays (about 1.5 Å).

Powers & Shefner (75) have investigated reduced vigor after autogamy in *P. aurelia* using very high doses. Kimball (76) has suggested that this reduced vigor is primarily due to gene mutations induced by the radiation and made homozygous by autogamy. Geckler (105) has presented evidence which suggests that this may not be the whole story. Powers and Shefner (75) found that the percentage of reduced vigor reached a maximum at about

50,000 r, but decreased somewhat at higher doses, and then started to increase again very slowly. A somewhat similar phenomenon was found by Powers & Raper (106) for nitrogen-mustard-treated paramecia. The meaning of the secondary decreases is not clear.

Kaplan (77, 78) has investigated the production of mutations in *Bacterium prodigiosum* and *Pencillium notatum* by photodynamic action of visible light, using the dye erythrosin. For the bacterium, he finds a two-hit curve for mutation induction (dwarf colonies) and a one-hit curve for killing. He concludes that the activation energy for mutation must be greater than 1.5 to 2 e.v., while for killing it is less. The probability of a killing hit as compared to a mutation hit is 3:1 for photodynamic action but 150:1 for ultraviolet. It is concluded that this may be due to the high nucleic acid content of the sensitive region for killing. From this, he concludes that death in bacteria cannot be looked upon as due simply to a lethal mutation. The relation of concentration of dye to mutation is a linear one, suggesting that one dye molecule is sufficient. For the mold, he finds that mutation follows a one-hit curve with either photodynamic action or ultraviolet, whereas killing shows a two- to three-hit curve for both. He concludes that the activation energy for mutation in the mold is less than 2 e.v. and so less than for the bacterium. He believes that the killing of mold spores may be due to haploid-lethal deficiencies and so to a mechanism different from that in killing of bacteria.

A number of investigations have been carried out on the induction of mutations in organisms grown in the presence of P^{32}. Bateman & Sinclair (79) and Blumel (80) have reported mutations in *Drosophila* and Thompson *et al.* (81) in barley. Bateman & Sinclair (79) believe that the ratio of visibles to lethals was higher than with x-rayed material, but offer no explanation. Gustafsson *et al.* (82) have investigated the effects of β-particles, positrons, and α-particles from a variety of radioactive isotopes upon growth and chromosome aberration production in barley and onion. The α-particles from radon apparently induced more dicentric bridges than did the others. Both King (83) and Rubin (84) have discussed the possibility that part of the mutational effect of P^{32} in the medium may be by way of the transmutation of incorporated P^{32}. Rubin (84) gives calculations for *E. coli* grown in the presence of P^{32} which appear to show that the increase in specific ionization as a result of concentration of the phosphorus in the bacterium cannot account for all the increase in mutations. Also the pattern of change is not readily understood in terms of ionization alone. Calculations indicate that transmutation may be involved. King (83) studied mutation production in *Drosophila* with P^{32} in the culture medium. A suggestion is made concerning a method to investigate the transmutation effect, but the suggestion apparently ignores the difficulties in calculating the internal dose of β-radiation.

Reverse mutation.—It has usually been accepted that gene mutations can be induced to undergo reverse mutation by x-rays, and a number of such cases have been reported for *Drosophila*. LeFevre (54) tested some of these same loci and was unable to find reverse mutation in fairly large x-irradiated

series. He was also unable to detect somatic reverse mutation of three different white alleles. He discusses possible reasons for this difference, including the possibilities that the previous reports involved contamination and that the particular mutant alleles which he used were not able to revert although others could. It should be noted that Giles (85) has found that certain, but not all, inositol-requiring mutants in *Neurospora* can revert. Reverse mutation in *Neurospora* has been investigated by several workers [reviewed by Horowitz (86)]. Lieb (87) has investigated reverse mutation in *E. coli* with ultraviolet.

Various effects.—Bonnier & Luning (88) using *Drosophila*, studied dominant lethals which they assume to be due to losses of parts of the chromosome. They found that the lethals increase with the time from irradiation to fertilization, and they assume that this is due to the greater chance that the broken ends will move apart before restitution can occur. They also found that a greater effect was produced upon the sperm of older males and suggest that this is because the sperm changes with age in such a way as to make restitution less likely.

McQuate (89) found a loss of chromosomes in *Drosophila* irradiated with ultraviolet. The loss was due either to breakage of the chromosome or to lagging. However, it could be shown that breakage, if it was induced at all usually must have been followed by union of the broken ends. Thus it seems improbable that terminal deletions could have been involved.

Rothfels (90) investigated the production of chromosome breakage in the grasshopper *Chloealtis conspersa* and gives quantitative data for amount of effect and time after irradiation at which various types become detectable. Slizynski (91) found that x-irradiation of *Drosophila* embryos leads to the production of partial chromosome aberrations in the salivary gland chromosomes. This is regarded as evidence for the polytene structure of these chromosomes, i.e., that each is composed of many strands of chromonema.

No attempt will be made to mention all papers in which radiation-induced mutations were used as tools. However, the extensive work of Plough (92) on radiation-induced mutations in *Salmonella* shows how it is possible to use this tool to investigate the genetics and biochemistry of bacteria. Reference should also be made to the reviews of Horowitz (86), and Tatum (93, 94) on *Neurospora*, Boivin (95) and Kaplan (96) on bacterial genetics, and Gottschewski (97) on microörganism genetics, in all of which, rather considerable sections are devoted to mutational research with radiation. Mention should also be made of the first report of an x-ray-induced mutation in a nematode by Thomas & Quastler (98).

Whittinghill (99) and Hinton & Whittinghill (100) have published reports of investigations of the effects of ionizing radiation upon crossing over in *Drosophila*. Whittinghill (99) found that 4,000 r of γ-radiation caused a distinct increase in crossing over in the region of the spindle attachment, while at the ends of the chromosome, crossing over was reduced. Coincidence was also increased near the center. Hinton & Whittinghill (100) report that

the distribution of the crossovers to different females suggests that oögonial cells were affected. Either there was a weakening of specific places in the chromosomes of the oögonia followed by crossing over at meiosis, or crossing over occurred in the oögonia.

Glass & Plaine (101) have continued the earlier studies of Glass upon the expression of the erupt gene and its suppressor in *Drosophila*. If embryos with the erupt gene and its suppressor are exposed to x-rays, the erupt character is expressed despite the suppressor as had been previously shown. The present paper demonstrates that this effect can be produced if eggs are irradiated shortly after fertilization, but not if either sperm or unfertilized egg are irradiated. They interpret this to mean that some gene product of the suppressor gene is produced very early in development and that this product can be inactivated by x-rays.

There have been several investigations of the inactivation by radiation of the self-reproducing cytoplasmic particle kappa. Kappa occurs in the ciliate *P. aurelia* and is responsible for the production by animals which contain it of a substance lethal to other paramecia. Once kappa is lost from the cytoplasm it cannot be formed *de novo*. Thus it is possible to analyze for its loss by investigating the number of animals which give rise to the clones lacking the killing power. Preer (102) investigated the inactivation of kappa by x-rays. From the dosage curve which was nearly of one-hit type, he was able to calculate an inactivation dose which agrees fairly well with the microscopically determinable size of approximately 0.5μ. Kimball (76) demonstrated that kappa can be inactivated by 2537 Å ultraviolet, and Geckler (103) showed that it can be inactivated by nitrogen mustard.

L'Heritier & Plus (104) investigated the inactivation of sigma, the self-reproducing cytoplasmic entity which controls carbon dioxide sensitivity in *Drosophila*. Sigma has many features in common with kappa but appears to have a very much smaller sensitive volume, 42 mμ, as compared with the very much larger size for kappa.

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SOME ASPECTS OF THE BIOLOGICAL ACTION OF HIGH ENERGY RADIATIONS

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Radiobiology embraces a diversity of interests. To understand its nature, we must contend not only with the subtlety and uncertainty of biology but also with the physicochemical events that are relevant to the absorption of concentrated packages of energy. While radiobiology is, implicitly if not explicitly, concerned with the action of all radiations on living systems, in practice, the high energy radiations command the greatest attention. Actually, all of the radiations are closely related, for to be effective each must function as activation energy whether this results from the highly specific molecular excitation with ultraviolet or from the more nonspecific transfer of energy by ionization and excitation with x-rays.

In this report, our interest will be confined to the high energy or ionizing radiations and we will be concerned, for the most part, only with contributions that have appeared during the past year. Radiation effects on genetic materials and on micro-organisms are treated elsewhere in this volume and will not be considered in detail here.

Complementing and highlighting the individual investigations during 1950 were several symposia devoted to radiobiology. The basic aspects of radiation effects on living systems was the subject of a symposium held at Oberlin College under the auspices of the National Research Council. Several sessions of the 6th International Congress of Radiology, the 50th Anniversary Celebration of the Discovery of Radium, and the annual meeting of the American Association for the Advancement of Science were likewise devoted to radiobiological matters.

Mode of Action

High energy radiations dissipate their energy in tissue by ionization and excitation. The dependence of biological effectiveness upon the specific ionization or ion density of a particular radiation lends strong support to the idea that its action is in some manner related to direct local release of energy, presumably through ejection of electrons from the atoms through which it passes. While the role of excitation is not well defined, it may constitute an important secondary, if not primary, process. An interesting aspect of the energy absorption is the relatively small absolute amount that is required to produce widespread effects. One thousand roentgens, a lethal dose for most mammals, corresponds to an energy absorption of only 2×10^{-3} cal. per gm. We may examine the problem in another way by computing the fraction of molecules within a cell that are likely to be modified as a direct result of the

radiation. In a cell containing about 10^{14} molecules, 1,000 r would be expected to ionize only 10^{7} molecules. Although it is likely that many more molecules will be affected indirectly in consequence of the energy transformations resulting from the absorption of radiation, the total number of altered molecules is probably a small fraction of those present within a cell. It would seem, moreover, that not all of the damaged molecules are of critical importance in the cell economy since most of these would be water molecules. These considerations raise the question of the localization and amplification of the early critical events. Although amplification could be accomplished by inactivation of genes or enzymes, by some disturbance in the synthesis or assembly of essential substrates, or by the formation of toxic substances, the nature of the early physicochemical events is obscure and poses the most formidable problem in radiobiology.

Two main concepts of radiation effects on living systems have been formulated. These are most frequently described as the theories of direct and indirect action and have been the subject of spirited discussion during the past several years. Direct action postulates that ionization occurs in specific molecules which constitute a sensitive region or vital target (1). This idea in its classical sense is compatible with the single hit type of effect that is characterized by its exponential relationship to radiation dosage, its independence of dosage rate, and the inverse relationship between its efficiency and ion density. It is perhaps best expressed in the effects on dried biological materials. While the linearity of a dose-effect curve strongly suggests a single hit action, it is worth noting that linearity per se does not necessarily constitute proof of such action (1, 2).

Both the direct and indirect concepts assume that chemical changes are induced by ionizing radiation, either by the destruction of important molecular species or by the production of substances that influence cell metabolism (3). The indirect effect assumes that the chemical changes are a result of highly reactive substances, mainly oxidants, that are formed at random in the aqueous environment and subsequently react with critical entities. Thus, localization of an effect within the system is secondary and depends upon the nature of the acceptors as well as upon the original distribution of ions, the number of reactive substances formed, and the kinetics of their diffusion. The indirect type of action is dose-rate dependent and varies directly with ion density. This also appears to be the case for certain multiple direct hit processes (4, 5). It has been shown that both direct and indirect actions may contribute to the early relevant reactions for specific effects such as gene mutations and chromosome breaks (6).

While survival curves may appear to reflect single or multiple hit events, the ion pairs need not occur in the sensitive sites. Moreover, if diffusion of free radicals or altered molecules can occur to any appreciable extent, the effective sensitive volume will be increased manifold. Tobias (7) relates local damage in a single vital area of a cell to its cross section, the number of reactive substances (radicals and intermediates) formed, and their coefficient

of migration and mean free path for chemical interaction. The diffusion factor has also been emphasized by Rajewsky (8). These considerations appear to explain the dependence of haploid yeast cell sensitivity on the rate of energy loss or linear ion density that has been observed by Zirkle & Tobias (9) as well as the exponential shape of the survival curve. The difference in the response of haploid (one hit) and diploid (multiple hit) yeast cells with increase in radiation dosage and the greater radiosensitivity of the former, which was described by Latarjet & Ephrussi (10) and confirmed by Zirkle & Tobias (9), may also be explained on this basis.

The abundance of water in biological materials and the demonstration of activated water reactions in simple chemical systems have led to much speculation concerning their implication for radiobiology. As pointed out by Weiss (11), irradiated water is essentially an oxidation-reduction system that consists primarily of free hydrogen atoms and hydroxyl radicals. The action of radiations on dissolved materials depends not only on factors such as solute concentration, pH, and temperature, but also on the initial spatial distribution of the ions. It has been suggested that free radicals may be formed in the ambient liquid even when ionization occurs directly in a biological particle and, moreover, that small targets may be more effective per unit volume than large targets since the probability of chemical change is greater when ionization occurs near the surface (12). Bonet-Maury (13) and Burton (14) have discussed the different mechanisms for the formation of peroxides by x-rays and alpha particles. Heavy particles produce peroxides in pure water (presumably from OH radicals), whereas with gamma and x-rays peroxides do not appear unless dissolved oxygen is present. Obviously, pure conditions do not obtain in biological systems where many acceptors are available for reaction with the decomposition products of irradiated water. Moreover, these products may not be of equal consequence on the inside and outside of a cell.

The relationship between radiation effect and chemical structure has been discussed by Dale (15). Substances of low molecular weight with special atomic grouping may show wide differences in their response to radiation. Weiss (16) has investigated the action of x-rays on amino acids, nucleic acids, and sterols. Ammonia is considered to be an important by-product of the reaction with nucleic acids as with amino acids. Barron *et al.* (17) continue to emphasize the important role of dissolved oxygen in many of the oxidations produced by ionizing radiations. The oxidation of thiols is reduced by two-thirds when irradiation with beta, gamma, or x-rays takes place in the absence of oxygen. The contribution of H_2O_2 is only of the order of 20 per cent. In contrast to the results with thiols, Barron & Bonzell (18) believe that the *in vitro* oxidation of reduced cytochrome-*c* is due only to the OH radicals that are formed in irradiated water. Irradiation in the presence of catalase or in the absence of oxygen does not alter its oxidation. Reduction of oxidized glutathione or of oxidized cytochrome-*c* by x-rays was not observed.

Butler and associates (19) and Ross (20) have described certain similarities in the mode of action of sulfur and nitrogen mustards and x-rays. Parallel physical changes in nucleic acids have been observed by Butler *et al.* According to Ross, free radicals, like the carbonium ions derived from mustard, are electrophilic reactants that can react with specific groups, such as the ionized carboxyl groups of proteins, to yield other electrophilic reactants. The radicals produced by radiation, or the carbonium ions from mustard, might in this way initiate a chain reaction that could account for the observed degradation of nucleic acids. Limperos & Mosher (21) have determined that x-rays are unable to depolymerize desoxyribosenucleic acid in the dry state, in ethylene glycol, or in a frozen aqueous solution. However, depolymerization occurs readily in aqueous solutions following x-irradiation or exposure to chemically generated free radicals. Thiourea affords effective protection against depolymerization which, in the case of x-rays, is considered to be mediated by activated water reactions.

Reduction in viscosity of vitreous and umbilical cord hyaluronate solutions as a result of x-irradiation has been observed by Schoenberg *et al.* (22) who also point out that the irradiated hyaluronate is stable in the dry state. The rate of enzymatic degradation of the irradiated solutions is lowered probably because of the marked decrease in average molecular weight. The activity of hyaluronidase solutions is also diminished by irradiation. These effects may bear some relationship to the action of radiations on tissues.

Although activated water reactions have been observed in a number of simple *in vitro* systems, demonstration of similar phenomena *in vivo* has not been an easy task. For example, the inability to detect an immediate oxidation of sulfhydryl groups in tissues obtained from heavily irradiated animals is consistent with theoretical considerations, which reveal that only an exceedingly small fraction of the available sulfhydryl reservoir could be oxidized even in the absence of the naturally occurring protective substances (23). Perhaps the most convincing evidence, admittedly indirect, in support of the *in vivo* effects of activated water comes from studies with anaerobiosis and with protective substances. The dependence of radiosensitivity on the degree of hydration, which has been demonstrated in seeds and isolated tissues, may also be interpreted in this light.

Deprivation of oxygen during exposure to gamma and x-radiation diminishes their action in a variety of biological materials. The implication of a reduced oxygen tension for radiosensitivity may be found in the experiments reported by Mottram in 1924 (24). The effects of anaerobiosis were subsequently described by Crabtree & Cramer (25) and the possible relationship of this aspect of radiosensitivity to the reactions of activated water was suggested by Thoday & Read (26, 27). More recently, anoxia has been shown to decrease the frequency of chromosome aberrations in *Tradescantia* (28) and sex-linked lethal mutations in *Drosophila* (29). Reduced oxygen tension has also been found to decrease the lethal action of x-rays in bacteria and fungi (30), in mice and rats (31), and in *Daphnia magna* (32). Anoxia has

also been shown to afford some protection to the frog against the lethal effects of x-rays (33). The early failure to increase the resistance of this species with anoxia may have resulted from some latent infection in the animals, since protection was observed subsequently when streptomycin was added to the water or the radiation dosage was decreased (34).

The resistance of living systems to x-rays is said to be the same whether anaerobiosis is induced by nitrogen, helium, argon, or hydrogen (28). A biological parallel to the radiochemical reactions involving oxygen in aqueous solutions may be the observation that oxygen lack does not significantly protect broad bean roots against growth reduction following alpha irradiation (27, 35). Oxygen deprivation would be expected to exert a negligible influence on peroxide formation by alpha rays.

Giles & Beatty (36) have observed that the increase in chromosome aberration frequency with x-rays is linear between 0 per cent and 10 per cent oxygen, after which the rise is somewhat more gradual, tending to level off above 20 per cent. The number of chromosomal deletions was also shown to be a function of the ambient gas pressure as long as oxygen was present. Experiments with hydrogen suggest that residual aberrations which are induced by x-rays in the absence of oxygen may be the result of a direct effect of the radiation on chromosomes. In this connection, the observations of Hewitt & Read (37) on bacteriophage are of interest. Under conditions in which inactivation was considered to arise from a direct action on the phage particles, there was no significant difference in the x-radiation effect on oxygen-free and oxygen-rich suspensions of bacteriophage.

Several chemical procedures that bear on the events associated with the oxygen effect have been employed. Cyanide exerts some protective action against x-rays in the mouse (38) but not in the rat (31). The failure of cyanide-induced anoxia to protect the rat and the protection afforded this species by anoxic anoxia have been taken to indicate that radiation injury is related to the tissue oxygen tension. On the other hand, it has been suggested that cyanide protects the mouse by inhibiting the formation of peroxides by x-rays and perhaps by forming a loose bond with sulfhydryl groups to prevent their oxidation. Also unexplained is the finding that para-aminopropiophenone enhances the resistance of mice and rats when it is administered before x-irradiation (39), while sodium nitrite, which produces a rather similar methemoglobinemia, gives equivocal protection (39, 40).

A number of oxidizable entities have the capacity to diminish the effects of x-rays. Patt, Smith, and associates (41, 42) have described a marked reduction of radiotoxicity in mice and rats after pretreatment with cysteine. Glutathione and 2,3-dimercaptopropanol (33) are also effective, while cystine, methionine, and ascorbic acid are without influence. Protection of mice and dogs with glutathione has also been reported by Chapman *et al.* (43, 44). Forssberg (45) notes that cysteine decreases the radiosensitivity of bacteria and also of guinea pig skin to local irradiation. Similar protection has been observed by Hollaender *et al.* (46) in *E. coli.* Massive near-lethal doses of

glucose given prior to irradiation are reported to enhance the survival of rats (47). Conversely, pretreatment with insulin augments cutaneous radiosensitivity in the rabbit, presumably because of hypoglycemia (48). Some degree of protection has also been seen with thiourea and dithiophosphonate in preliminary experiments (49, 50),

It is consistent with the concept of the mode of action of these substances that they must be given before irradiation to be effective. Cysteine may about double the 30-day LD_{50} for rats, provided it is administered before exposure (41, 42). Its injection immediately following irradiation does not alter toxicity. It seems reasonable to infer that the radiation events against which cysteine protects are completed when the exposure is terminated and that, for all practical purposes, these reactions are not reversible. Although some improvement in survival has been observed in a small series of rabbits after treatment with cysteine plus ascorbic acid during the first two post-exposure hours (51), this has not been verified in either rabbits or mice (52). The mechanism of the protective action is unknown. It appears that cysteine is acting as a reducing agent, either intra- or extracellularly. In this capacity it may increase resistance to irradiation by competing for the products of activated water or by altering metabolic pathways within the cell (23). It is of interest that the protection afforded by cysteine shows some proportionality to the dosages of cysteine and radiation (42).

It is not known whether reducing substances and anaerobiosis protect all systems in the same manner. Holmes (53) observed that x-ray inactivation of ribonuclease in dilute aqueous solution was prevented by glutathione but not by oxygen lack. However, it is noteworthy, though possibly fortuitous, that the resistance of the rat to the acute lethal action of x-rays is increased to the same degree by anoxic anoxia and cysteine. Moreover, additivity has been observed in bacteria. In the studies of Hollaender *et al.* (46) radiosensitivity of *E. coli* was reduced beyond the value obtained with anoxia alone when cysteine was present during the exposure. On the other hand, there was no significant increase in survival when cysteine was added to anaerobically-grown bacteria irradiated in the absence of oxygen. These findings lend further support to the idea that radiosensitivity may be influenced by the metabolic state as well as by the aqueous environment. Of interest in this connection is the finding of an increased number of dominant lethal mutations in *Drosophila* irradiated in oxygen at 2°C. over those treated in oxygen at 27°C. (29). This effect may perhaps be related to the higher oxygen tensions within the irradiated sperm at the lower temperature.

Evaluation of temperature effects during irradiation is complicated since temperature may alter the quality as well as the quantity of cellular activity which, in turn, may modify the response to irradiation. Further, reactions of injury and of recovery must follow rapidly the primary events that are associated with the absorption of energy, and it is highly probable that these secondary metabolic reactions appear in some degree even before the irradiation is terminated. Since the time course and temperature coefficients

of the subsequent biochemical changes may vary for the different effects and systems, it is not surprising that many types of temperature responses have been described. While it is true that fern spores and certain pollens show an enhanced radioresistance at liquid air temperatures, perhaps mainly because of altered formation and diffusion of free radicals, there is reasonable evidence that less extreme temperature changes do not directly influence the immediate radiation reactions in living systems. Further support for this is derived from the work of Allen, Schjelde & Hochwald (54, 55) in which variation in ambient temperature from 0 to 22°C. during irradiation did not alter appreciably the response of the tadpole. Temperature independence over this range is consistent with the concept of indirect as well as of direct action since the free radicals must have zero or nearly zero energies of activation. The events subsequent to irradiation appear to be rate sensitive, however. Yet, since recovery may also be influenced, the ultimate outcome is not always changed.

Consistent with the temperature effects are the observations of Smith & Smith (56) in which treatment of mice with desiccated thyroid both before and after irradiation gave the same enhanced effect as treatment only after the exposure. Thyroid feeding begun one week before irradiation and terminated on the day of exposure did not modify lethality. Potentiation of toxicity when thyroid is given after irradiation may be related to the increased oxygen consumption. In contrast to these findings, Haley, Mann & Dowdy (57, 58) have reported little difference in the lethal response to x-rays of normal, presumably hypothyroid, and hyperthyroid animals. However, the extent to which their procedures modified metabolic rate was not stated.

Biological Effectiveness

While all of the ionizing radiations produce more or less similar physiological effects, their efficiency varies considerably and depends not only upon the energy absorbed per unit of volume and of time but also upon its distribution within the organism. Further evidence along these lines has been presented by a number of investigators. Gray & Read (59) have found that for reduction of the mitotic index in broad bean roots, alpha rays are less efficient than either neutron or gamma radiations when all doses are measured in ergs per gram. The relative efficiency for gamma rays, neutrons, and alpha rays was 1:2.1:0.6 in contrast to the effectiveness of these radiations in killing the roots which was 1:9:9. The observed ratio for neutrons and alpha rays in regard to mitotic inhibition is considered to be the inverse of the ratio of their linear ion densities which is thought to be suggestive of an effect brought about by a single alpha particle or recoil proton.

For most systems, biological effectiveness increases with increase in linear ion density. Thermal neutrons have been found by Conger & Giles (60) to be about 11 times as effective as x-rays for producing chromosomal aberrations in *Tradescantia* microspores, and 200 k.e.v. x-rays are more effective than

high energy electrons from the betatron for inducing a number of biological effects (61 to 64). The gamma to x-ray ratio of effectiveness for lethality in mice varied from 2.1 to 3.6 in the experiments of Bonet-Maury & Patti (65). These ratios seem rather high. Two hundred k.e.v. x-rays are only about 1.3 times as effective as 20 m.e.v. x-rays that have a specific ionization comparable to that of hard gamma radiation (61). Snyder & Kisieleski (66) have determined that 200 k.e.v. x-rays are 1.4 times as efficient as sodium-24 beta rays for acute killing of mice, but the true ratio may be somewhat lower since the x-radiation was given in about 30 minutes while the beta radiation was given over a period of several hours. Wachsmann (67) and Kepp (68) believe that there are also qualitative differences in the action of high and low energy radiation. Additivity of the various ionizing radiations has been discussed by Zirkle (69). When the energy distribution is similar and the exposure time relatively brief, complete additivity is usually obtained, suggesting that the events that are directly responsible for the observed effect are identical.

The efficiency of fractionated radiations appears to be influenced by recovery mechanisms (61, 70). Quastler & Lanzl (61) believe that this may account for the lower relative efficiency of 20-million-volt roentgen rays with fractionation as compared with the greater relative efficiency of neutrons under similar conditions. The size of each fraction as well as the over-all exposure time influences acute lethality in x-irradiated mice. Of these two factors, the former is considered to be the more important by Ellinger & Barnett (71). Repeated total-body irradiation of mice with low dosages was found by Bloom (72) to result in sensitivity maxima and minima of the duodenal epithelium. The acquired radioresistance of the duodenal crypt cells after 10 or more daily exposures to 60 r was indicated by negligible amounts of debris and persistence of mitotic activity even with total accumulated dosages of 2,100 r and also by the partial protection that was manifest when a larger single dosage (200 r) was given within a week of termination of the daily exposures. It would appear that the increased tolerance under these conditions cannot be explained solely on the basis of recovery mechanisms.

For the majority of acute biological responses, the effectiveness of a given dose decreases as the rate of exposure decreases, at least within certain limits. Consistent with this is the observation by Casarett (73) of a diminished mortality of rats and dogs with decrease in the intensity of single dosages of x-radiation. Another aspect of the intensity-duration factor is the production of different effects with the same total dose. Karnofsky *et al.* (74, 75) have reported early deaths, within 24 hours, in chick embryos and young chickens when dose rates above 5 to 10 r per min. are employed. Early toxicity is relatively independent of a total dose above 800 to 1,000 r. From dose fractionation studies it appears that the over-all time of exposure is more important than dose rate in eliciting these particular effects (76). These observations have been extended by Stearner and associates (76, 77, 78)

who present evidence indicating that early deaths in chicks and ducklings may be related to renal failure.

The survival of mice under duration-of-life exposures to x-rays at different dose rates has been determined by Sacher (79) who points out that it may be possible to separate physiological injury processes into their basic components by analysis of the various patterns of lethality.

The response to radiation depends upon the portion of the cell or organism that is irradiated. There is reason to believe, moreover, that injury to specific sites is more severe after a total-body exposure than after local irradiation. Jolles (80) has made the interesting observation that the severity of the erythematous reaction of skin is related to the size of the radiation field and that two fields a distance apart show less injury than areas that are closer together. A diffusible substance has been postulated to account for the "reciprocal vicinity effect." Partial irradiation of the frog's corneal epithelium with 3,600 r has been found by Strelin (81) to produce the same over-all inhibition of mitotic division as total irradiation of the cornea with 900 r. With low dosages, recovery is faster after partial exposure, presumably because of some chemical interaction between the irradiated and adjacent nonirradiated area.

Shielding of the head or of the extremities in rats (82) and in dogs (83) decreases the severity of an otherwise lethal effect. In a small series of dogs, Allen (83) found that head shielding alone reduced mortality from a completely lethal dose by about 75 per cent. With the abdomen shielded, 1,950 r are required to kill 50 per cent of x-irradiated rats within 28 days, while with only the abdomen exposed 1,025 r suffice to kill an equivalent number (84). Bond *et al.* (84) suggest that different mechanisms may contribute to mortality, depending upon the region that is irradiated.

Jacobson *et al.* (85, 86) have extended their observations on the effects of spleen protection on survival and on hematopoietic recovery in x-irradiated mice. This effect is not restricted to the spleen, for shielding of the appendix in the rabbit also permits a more rapid regeneration of irradiated hematopoietic tissue. While the mechanism of this recovery is not well understood, it has been suggested that the spared mesenchymal tissues may supply a humoral substance that facilitates regeneration of blood-forming tissue. In contrast to protection by shielding is the synergism that results when certain radioisotopes which differ in localization are administered in combination. Friedell & Christie (87) have observed that lethality is potentiated, when the reticuloendothelial system of rats is irradiated with colloidal gold-198 and the bone marrow with phosphorus-32.

Effects on Growth

A type of reciprocal relationship exists between the ionizing radiations and growth processes. Proliferative activity is usually associated with radiosensitivity, and it is well known that the most dramatic effects of radiations are related to its influence on growing or developing systems.

Knowlton & Widner (88) have utilized the effect of x-rays on cell division to determine the mitotic time of different tissues. This was derived by delaying mitosis in early prophase with x-irradiation. Differences in the mitotic indices among the various tissues were found to be primarily a consequence of the variations in intermitotic times. An increase in the size of irradiated yeast cells has been observed by Brace (89). Cell enlargement is accompanied by a nonselective increase in cell constituents and may perhaps be attributed to the temporary inhibition of mitosis resulting from irradiation. Methylthiouracil has been employed by Montag (90) to facilitate detection of nuclear changes in the follicular cells of the irradiated thyroid. X-irradiation of the rat thyroid with 1,500 r results in degenerative changes in the nuclei that become apparent when mitosis is accelerated as a result of methylthiouracil administration. Tritium-treated cultures of chick embryo fibroblasts have been observed cinematographically by Stroud & Brues (91). Inhibition and delay of cell division with a subsequent increase in the number of abnormal mitoses and of degenerate cells were consistent findings. The highest percentage of abnormal mitotic cells was found in metaphase. With the lower rates of exposure (167 r.e.p. per hr. in contrast to 417 r.e.p. per hr.), a constant level of abnormal mitosis was not reached for some hours, suggesting perhaps that under these conditions abnormalities were manifest only after the cells had passed through one division.

The growth of squid larvae is immediately inhibited by 5,000 r and dosages of 800 r lead to severe changes in the retina according to Rugh (92) who has also determined the influence of x-rays on squid larval tropisms. Inhibition of growth and varying degrees of degeneration and other developmental defects are seen in the tails of young axolotls after local x-irradiation (93). Developmental effects in wasps exposed to beta radiation immediately prior to hatching or during the early larval period have been reported by Dent & Amy (94). Sterility was the most prominent symptom in irradiated animals reaching adulthood. Comparison of adult wasps developing from x-irradiated prepupae and pupae revealed a greater number of haploid males with structural malformations than diploids of either sex (95). In conformity with the previously cited observations on yeast cells (9, 10), x-rays were also found to have a greater lethal effect upon haploid than upon diploid forms, suggesting that the number of chromosome sets may be a substantial factor in radiosensitivity.

Brunst (96) has reviewed the effects of x-radiation on limb regeneration in amphibia. Postamputation irradiation of the regenerating limb leads not only to an arrest of the regenerative process but also induces a rapid decrease in size or reduction of the x-rayed regenerate. A similar reduction occurs in developing limbs and tails of irradiated amphibian larvae. By local irradiation it is possible to destroy regenerative ability in the proximal and distal portions of a limb while preserving this capacity in a small nonirradiated intermediate area. Transplantation of a nonirradiated regeneration bud into an irradiated site leads to normal regeneration. However, the reverse situa-

tion does not permit regrowth. Of interest is the observation that tissue and organ differentiation in the irradiated amphibian may be completed despite cessation of cell division. Parts of x-irradiated amphibian embryos have been transplanted to normal embryos by Perri (97) who notes that such procedures may permit longer survival of the exposed organ. Conversely, transplantation of nonirradiated parts to irradiated embryos does not seem to affect their development.

Radiation effects on the pre-implantation stages of the mouse embryo were investigated by Russell & Russell (98) who observed a high prenatal fetal mortality but only a negligible incidence of abnormalities in animals surviving to term. The earliest stages after mating were found to be most sensitive. When the pregnant mouse was exposed during the postimplantation stages, the relative magnitude of the effects was reversed, abnormality exceeding mortality. Malformations of the skeletons of animals irradiated in utero have been described by Russell (99). The great sensitivity of developing neuroblasts in mouse and rat embryos during the latter two-thirds of pregnancy is reported by Hicks (100) who notes that 150 r delivered to pregnant animals results in extensive destruction of neuroblasts with severe malformations of the brain, whereas extraneural lesions are absent with this dosage. A somewhat different approach is described by Wilson & Karr (101) who irradiated selected implantation sites in pregnant rats without exposure of the mother. Exposure to 200 r on the ninth day was completely lethal while 400 r were required on the tenth day of gestation. This may be related to implantation of the embryo. Development was also altered more severely following sublethal irradiation on the ninth rather than on the tenth day. The developing nervous system, especially the eye, appeared to be the most susceptible site.

The chick embryo manifests an increased sensitivity to the acute toxic effects of x-rays during the third to seventh day of incubation and is most sensitive at the eighth to tenth day after which its response is stabilized at a slightly more resistant level (74). Depression of growth is also related directly to the age of the chick embryo at the time of irradiation. Of interest here is the observation by O'Connor (102) that the number of dividing cells in the nonirradiated chick embryo decreases markedly between the third and eighth day of incubation. Oxygen consumption is unchanged but a threefold decrease in aerobic glycolysis is seen at this time. Jacques & Karnofsky (75) find that the LD_{50} for delayed deaths is higher for the chick embryo than for the chick and suggest that this may be due, in part, to the absence of infection in the egg.

Bless (103) has examined the relationship between the bioelectric potential (potential difference between the tip of the coleoptile and the seed coat) and coleoptile length in x-irradiated wheat seedlings. Each parameter decreases with increasing dosage although the diminution is not exactly parallel. The effectiveness of the radiation varies with the age of the seed at the time of exposure, the day-old seed being the most sensitive at 25°C. Since

the potentials in a given group of seedlings may vary considerably, presumably because of the wide differences in cell activity at a given time, the usefulness of such measurements is limited unless large groups are employed.

The influence of x-rays on linear growth in plants has been followed by Quastler & Baer (104) who observed a reduction in the capacity of *Mung* beans to initiate and complete growth. From an analysis of the dose-response relationships, it appears that growth initiation (cell division) is more radiosensitive than growth completion (cell elongation). The effect of ionizing radiation on auxin synthesis is of interest in this connection. This is being investigated by Gordon (105) who finds that depression of free auxin levels following low dosages of radiation may be attributed primarily to interference with the process of auxin formation. Exogenous auxin supplied prior to irradiation to grass shoots unable to synthesize the hormone allows growth to continue normally until the auxin supply is completely utilized.

Abnormalities of osteogenesis and odontogenesis, including failure of root formation, occur when colloidal radiogold is injected adjacent to the jaw of the immature mouse (106). Arkin & Simon (107) have observed that 1,000 r delivered to one side of the spine of young rabbits result in a structural scoliosis. Asymmetrical irradiation of the spine leads to unequal bone growth and wedging of the vertebral bodies. Radiophosphorus in sublethal dosage has been shown by Kligerman (108) to retard weight gain and bone growth in 21-day-old rats. However, the effect on growth is temporary and ceases when the concentration of P^{32} in the body falls below a threshold value. There were no differences in size, weight, and appearance between the controls and injected animals that reached an age of about 300 days. A marked increase in the calcified zone adjacent to the epiphyseal line was seen several weeks after lethal dosages of P^{32} (3,600 μc. per kg. repeated at 4 weekly intervals). Koletsky *et al.* (109) have shown that bone tumors may develop as a late effect in rats receiving large dosages of radiophosphorus. An atypical proliferation of bone, possibly a precursor of the malignant change, was noted in these animals.

Enzymes and Metabolism

The aberrations in cell chemistry that follow irradiation are not easily resolved since the properties of radiation and the structure and properties of biologically important molecules are still obscure. From energy considerations and the widespread nature of radiation damage there is reason to believe that the primary disturbance centers around enzymes, genes, and other key molecules that are involved in the assembly and synthesis of essential substrates. Presumably, certain of these entities are inactivated or modified by direct ionization and excitation and/or by the products of irradiated water. It has been postulated by Barron (110) that the critically involved enzymes are those requiring sulfhydryl groups for their activity and that these are reversibly oxidized by low dosages and irreversibly denatured by

higher dosages. Unfortunately, in vivo experiments have as yet yielded little direct evidence in support of this attractive hypothesis.

Inhibition of reactions known to involve —SH enzymes was first observed by Barron *et al.* (111) in tissue slices prepared from x-irradiated animals. Recently, Dinning and his associates (112) have found that exposure of mature hens to 300 r markedly reduces the endogenous respiration of bone marrow and the activities of choline oxidase and of succinoxidase, enzymes that require —SH groups for their function. Yet, Le May (113) has failed to detect significant inactivation of certain —SH enzymes in vivo with moderate dosages of x-rays. Inhibition of the succinoxidase system in rat kidney homogenates was not observed nor was there any difference in the respiration of kidney slices from irradiated and control animals with pyruvate or succinate as substrates. Dubois, Cochran & Doull (114) have also been unable to detect significant changes in succinic dehydrogenase and adenosinetriphosphatase when specific assays for these enzymes were made on tissues taken from mice exposed to gamma rays. Although, in their experiments, irradiation did not alter the capacity of liver and kidney slices to oxidize malate, there was some inhibition of the oxidation of pyruvate and glucose.

While —SH enzymes may, therefore, be inhibited by ionizing radiations under certain conditions, their selective inhibition is open to question. Moreover, it is not known whether changes, when observed, are the cause or the effect of morphologic injury and cell death. In this connection, it is worth noting that there is no demonstrable change in the oxidizable sulfhydryl content of tissues immediately after irradiation (115, 116, 117). An apparently nonspecific reduction of available sulfhydryl groups may be observed several days or weeks after irradiation (116, 117).

Total-body x-irradiation of mice with 800 r has been shown by Feinstein and associates (118) to reduce liver catalase. Significant reduction was first observed 24 hours after the exposure. Of interest is their observation that injection of hydrogen peroxide resulted in a much more rapid decrease, within 2 min., in mouse liver catalase, perhaps rendering unlikely the notion that hydrogen peroxide formed by x-radiation is the agent directly responsible for catalase destruction. After sublethal x-irradiation of the rat with 500 r, Ludewig & Chanutin (119) were unable to detect significant changes in the nonmercapto enzymes of liver. Similar activities and distributions were obtained in liver cells and in liver connective tissue from control and irradiated rats for catalase, esterase, arginase, rhodanese, and alkaline phosphatase.

An initial increase followed by a decrease in the alkaline phosphatase activity of plasma has been observed in rats after single or multiple total-body exposure to x-rays (120). Decrease in plasma alkaline phosphatase activity may be attributed to anorexia, for rather similar changes are observed in fasted controls. Phosphatase activity is said to be increased in the thymus and spleen but not in the liver and kidney. Doyle (121) has failed to

detect any striking changes in the acid or alkaline phosphatase content of the rabbit appendix.

The aspartic-glutamic transaminase content of tissues from x-irradiated animals is not changed appreciably according to Tonhazy *et al.* (122). The possible relationship between pyridoxine deficiency and x-ray injury has been investigated by MacFarland and associates (123). Deprivation of pyridoxine does not increase the susceptibility of rats to x-radiation nor does the latter alter the concentration of pyridoxine in the livers of deficient or of control animals.

Immediate and delayed effects have been seen in desoxyribosenucleic acids prepared from the thymuses of rats that were irradiated with 1,000 to 2,000 r (124). The immediate effect, a splitting off of purine bases, was not prevented by the prior injection of thiourea, whereas the depolymerization noted at 24 hours was somewhat minimized by such treatment, suggesting that the delayed effect may possibly be initiated by activated water reactions. A remote or indirect effect of irradiation on nucleic acid formation was reported by Kelly & Jones (125) who used P^{32} to determine desoxypentose nucleic acid turnover rates in the tumors of mice after intravenous or intramuscular injections of radioyttrium colloids that were shown to localize in liver or muscle depending upon the route of administration.

An initial decrease in the oxidative capacity of the x-irradiated diapause egg for several days followed by an increase has been described by Tahmisian & Adamson (116) who find that the oxidase activity after the early depression is greater with 25,000 r than with 200,000 r. This may be related to their previous observations that negative growth and oxygen uptake also varied inversely with x-ray dosage.

Metabolic reactions after irradiation of the intact animal may result from action of radiation on enzyme systems, deranged synthesis or assembly of essential substrates, altered gastrointestinal, hormonal, and renal function, and the products of tissue breakdown. Certain metabolic consequences of irradiation were described as early as 1907 by Edsall & Pemberton (126) who interpreted clinical radiation sickness as a toxic reaction to tissue breakdown. While it is likely that tissue breakdown products contribute to the early shock reactions with massive irradiation, their role with smaller dosages is not well-defined. In this connection, Venters & Painter (127) have found that the sensitivity of irradiated animals to histamine, adenosine, and trypsin increases during the first few hours after exposure. Maximal changes in sensitivity are related in time to other physiological findings and may be a function of tissue damage.

The tissue breakdown associated with irradiation as with starvation does not result invariably in an elevated metabolism. While direct evidence of an increase in the metabolic rate of rats following whole body irradiation has been presented by Kirschner *et al.* (128), the changes in oxygen consumption do not coincide with weight loss. Other investigators have been unable to verify the increase in metabolic rate in rats and mice (33, 56), and have

found, moreover, that body weight changes appear to be related directly to the anorexia (33). The absence of any profound changes in metabolism of the intact animal in the presence of possible alteration in the endogenous respiration of radiosensitive tissues is not unreasonable, since the tissues that account for most of the oxygen consumption are notably radioresistant. Apparently, the tissue breakdown products resulting from moderate irradiation do not result in an appreciable over-all increase in metabolism, perhaps because of their rapid excretion or slow release, the associated inanition, or other as yet unknown factors.

Blood

The blood and the blood-forming tissues continue to constitute an important focus in radiation research. From morphological studies, it may be seen that changes in the peripheral blood cells, in general, parallel the alterations in the bone marrow, lymph nodes, and spleen. While the site of action of radiation appears to be mainly in the blood-forming organs, indirect effects on hematopoietic tissue and direct effects on the morphological constituents of blood have also been observed. Changes in the peripheral blood and bone marrow have been described by Betz & Lecomte (129) following heavy local irradiation of the hind paws of rabbits. Zimmer (130) presents a variety of peripheral blood effects that apparently depend upon the area that is irradiated.

Thermal fragility of rat erythrocytes has been shown by Goldschmidt and associates (131) to be elevated within the first few hours after a total-body exposure to 600 r. It is not known whether this represents a direct effect of x-rays on the red cell. Sheppard (132), using analytical as well as tracer procedures, has studied the sodium and potassium equilibria of human red cells in vitro. After irradiation, potassium is lost from erythrocytes and quantitatively replaced by sodium with little osmotic disturbance. With 20,000 r the mean rate of potassium loss is about 1 per cent of the initial cell potassium per hour. Although the rate of entry of potassium into the cell is only slightly depressed by x-rays, the reverse rate from cells to plasma is greatly accelerated. Using the electron microscope, Zocek & Rosenberg (133) observed changes in the appearance of the red cell membrane after the exposure of blood to 24,000 r. The size and shape of the cell membrane was apparently unaltered by the radiation.

Rosenthal *et al.* (134) have related bone marrow changes to peripheral blood counts. Formation of new cells from reticulum cells was completely inhibited for the first nine days following total-body x-irradiation of rats with 700 r. There was marked destruction of the erythroid elements in the bone marrow, while the myeloid cells showed mainly an accelerated maturation. The latter may account for the transient granulocytosis that is seen in some species during the first day after irradiation. Further evidence of the great radiosensitivity of the erythrocytic precursors is given by Hennessy & Huff (135) who have demonstrated a depression of tracer iron uptake by red cells

after total-body dosages of only 5 to 25 r. With a dosage of 250 r uptake is decreased by a factor of 10. The greatest depression of erythroid activity occurs about 1 day after irradiation. An early decrease in megakaryocytes has been observed by Roofe *et al.* (136) following the injection of radium chloride into rats. Megakaryocyte destruction is reflected by an early increase in blood platelets followed by a decrease. The reappearance of platelets is not well-correlated with megakaryocyte regeneration, possibly because the young forms do not fragment readily.

Stearner (137) reports that the relative radiosensitivities of the leucocytes are similar in the amphibian and mammal. The response occurs more slowly in the former and may be related to its lower rate of metabolic turnover. The peripheral blood response in rats and dogs following acute and chronic total-body exposure to x-rays has been related to radiation dose by Ingram & Mason (138, 139). They point out that changes that occur with small doses can be demonstrated only statistically. Consistent differences between survivors and nonsurvivors were not seen in their experiments. With chronic as with acute exposures, lymphocytes appear to be the most sensitive while the red cell is the least sensitive element in peripheral blood.

Lymphocytes with bilobed nuclei have been described by Ingram & Barnes (140) in cyclotron personnel as well as in experimental animals exposed to doses of cyclotron neutrons that were said to be considerably below the accepted tolerance values. Watts & Matheson (141) looked for, but failed to find, a change in the number or frequency of the refractile granules in lymphocytes of persons treated with radioiodine or exposed to x-rays. Snell *et al.* (142) were also unable to detect any significant hematologic changes in persons subjected to the atomic bomb two years previously. According to Mossberg (143), the blood platelets are relatively resistant to many external factors and afford a reasonable index of exposure to radiation. A decrease in platelets was seen in 7 of 24 persons engaged in radiologic work. In this connection, Macht & Macht (144) have ascribed phytotoxic properties to blood sera obtained from x-ray personnel. The incidence of leukemia in radiologists over a 20-year period was compiled by March (145) who found that leukemia occurred more than nine times as frequently in radiologists as in nonradiological physicians. While Lorenz (146) also observed leukemia in mice following acute or chronic total-body irradiation, the incidence was not increased in guinea pigs and rabbits. He questions the view that chronic irradiation, especially of the type encountered by radiologists, leads to an increase in the incidence of spontaneous leukemia in man.

Abnormal bleeding is usually, but not always, associated with the panhematopenia of acute irradiation. The bleeding tendency has been variously attributed to thrombocytopenia, blood vessel damage, and the presence of a circulating anticoagulant. It is probable that each of these factors contributes to radiation hemorrhage, though to a different degree depending upon species and conditions of irradiation. While hemorrhage is an almost invariable feature of the acute radiation syndrome, the extent and distribution of bleeding

may vary considerably among the different species and also among animals of the same species. The rabbit, in contrast to the dog and guinea pig, is considered by Rosenthal & Benedek (147) to show a mild hemorrhagic response to irradiation. The coagulation defect in the x-rayed rabbit is attributed chiefly to the thrombocytopenia. An increase in clotting time of some 60 per cent has been seen by Haley & Harris (148) in the irradiated guinea pig. Cronkite (149) has reported a hemorrhagic syndrome characterized by an increase in vascular fragility, thrombocytopenia, and ulceration in goats and pigs exposed to the atomic emanations at Bikini. Prolongation of the clotting time and the presence of a circulating anticoagulant were infrequent findings. This is at variance with earlier observations of a heparin-like substance in the blood of irradiated animals. Some of the disagreement may be attributed, perhaps, to differences in experimental technique.

A number of procedures has been employed in an attempt to modify the hematologic response to radiation. Reference has already been made to the work of Jacobson *et al.* (85, 86) on the effects of spleen protection on survival and on hematopoietic recovery. Huff *et al.* (150) have followed the distribution of tracer doses of iron-59 in rats exposed to a sublethal dose of x-rays with and without spleen shielding. Although similar clinical signs and loss of body weight were observed in both groups, there were impressive differences in the distribution of radioiron. In animals with protected spleens, the time-concentration relationships of the tracer in the spleen were almost identical with those noted in the bone marrow of the nonirradiated controls. This was not observed in animals without spleen protection and points to the capacity of the shielded spleen to undergo a functional metaplasia after x-irradiation. The effect is apparently not due to red blood cell destruction or to anemia but rather is considered to be related to a rise in the concentration of hematopoietic precursors in the plasma consequent to their lack of utilization by the irradiated bone marrow. Along these lines, the transplantation of normal marrow to irradiated rabbits and dogs was attempted by Rekers, Coulter & Warren (151). Marrow transplants to intra- or extramedullary sites were without appreciable benefit to the irradiated animals.

A single injection of cysteine immediately prior to exposure of the whole body of rats to x-rays was found by Patt *et al.* (152) to modify radiation-induced hematologic changes. Depression of the heterophils and lymphocytes was less severe and recovery more rapid. A mild transient anemia was noted in the protected animals in contrast to the severe erythrocyte depression in the irradiated controls. On the other hand, Hennessy *et al.* (153, 154), employing the uptake of radioiron in the red blood cells as an index of erythropoietic activity, failed to observe a protective effect of intravenous cysteine or subcutaneous glutathione in the irradiated rat. However, in their experiments the radiation dosage was above the threshold point of maximal change (135). The significance of the failure to observe protection with the radioiron technique under these conditions is, therefore, open to some question.

Single or multiple doses of vitamin B_{12} do not influence radiation leuco-

penia in rats according to Carter *et al.* (155), but administration of a vitamin P compound for several days before and for periods of one to three weeks after irradiation greatly enhances their survival (156). Vitamin P is considered to prevent the increased capillary fragility that is associated with radiation injury.

P^{32}-tagged erythrocytes and conventional Evans Blue techniques have been utilized by Storey, Wish & Furth (157) to determine cell and plasma volumes in irradiated animals. With 1,000 r in the rabbit, there is a parallel decline in cell and plasma volume on the third day. By the tenth day, however, plasma volume rises, reaching a level about 10 per cent above the normal during the third week when the red cell volume is decreased by about 40 per cent. The total blood volume is, therefore, only slightly diminished (by 10 to 20 per cent) following total-body irradiation in the lethal range.

Kohn (158) has looked into some of the possible mechanisms of the plasma changes in guinea pigs following a single total-body exposure to x-rays and has noted some discrepancies that exist between the radiation syndrome and the alarm reaction in regard to the character and time course of the effects. Glucose, cholesterol, and nonprotein nitrogen were increased and total protein fell during the first few days after irradiation. A rise in the albumin-globulin ratio was attributed to the presence in the plasma of a nonprotein material that was extractable with ether (159). Hyperglycemia and a decreased glucose tolerance have also been seen by Lourau & Lartigue (160) in the x-irradiated guinea pig.

Electrophoretic patterns of the plasma proteins of irradiated rats were followed by Gjessing & Chanutin (161) who also determined the nitrogen and lipid contents of the four plasma fractions. Variations from the control were minimal with sublethal exposures. Many of the changes with lethal dosages were similar to those found after thermal injuries and after injections of turpentine or of adrenal cortical hormones, a further indication of the nonspecificity of many of the radiation effects.

Studies of the thoracic duct lymph of irradiated dogs have been reported by Brown *et al.* (162). Uric acid and nonprotein nitrogen were elevated in lymph, but not in plasma, within 4 hr. of irradiation at which time a sharp drop in leucocytes was manifest. Sugar and chloride levels in the lymph were not altered during the 132 hr. of observation but lymph protein decreased.

Immunity and Infection

It is well known that total-body irradiation decreases resistance to infection and interferes with immune reactions. The problem of radiation-induced infection has been the subject of intensive investigation in recent years and it now seems clear that enterogenous invasion can be a substantial factor in radiation morbidity and mortality. Miller and his associates (163) have studied blood and spleen cultures from mice that received total-body x-radiation. They observed a bacterial infection of intestinal origin that reached its apogee during the period of greatest mortality. Subsequent work

by the same group (164, 165) revealed that the mortality of irradiated mice could be reduced with antibiotic therapy. Among the antibiotics tested, streptomycin and terramycin afforded the most effective protection to mice. Rather similar observations were made by Howland *et al.* (166) who found that antibiotics given to rats after lethal x-irradiation resulted in almost complete alleviation of the diarrhea and prolonged survival by about one week. Gram negative organisms normally occurring in the intestinal tract were suppressed. Some reduction of morbidity and mortality with aureomycin therapy was also noted in irradiated dogs. These findings have been amplified in work from the same laboratory by Furth & Coulter (167). In dogs exposed to 450 r, aureomycin reduced mortality from 58 per cent to 44 per cent and prolonged survival by more than one week. Gastrointestinal hemorrhage and ulceration were minimal in the treated animals but the hematologic picture was identical to that in the irradiated controls. The latter, however, showed a higher percentage of positive blood cultures. A somewhat lower incidence of bacteremia is seen in dogs than in mice, but even in this species infection appears to be related to mortality in animals surviving the first two weeks of irradiation. Antibiotics are also efficacious in certain types of radioelement poisoning. Streptomycin and penicillin, in combination, have been shown by Koletsky & Christie (168) to be effective in reducing mortality of rats given lethal dosages of radiophosphorus.

Burrows *et al.* (169) have shown that total-body irradiation of guinea pigs with 150 r results in a generalized tissue invasion by cholera vibrio from the original focus of infection in the bowel. This is not observed in similarly infected nonirradiated guinea pigs. The intensity of the enteric infection in the irradiated animals appears to be related to the decrease in coproantibody titer. Burrows has suggested that a similar decrease in titer may account for the bacteremia that is seen in the radiation syndrome, if natural immunity to intestinal organisms is related to the coproantibody response.

Recently, Schechmeister & Bond (170) have found a considerable incidence of bacteremia and death in mice exposed to sublethal dosages of x-rays and subsequently inoculated with live avirulent, or even dead, organisms generically different from the normal intestinal flora. Schwab *et al.* (171) have employed x-radiation to inhibit the formation of precipitins for whole bovine serum and bovine serum gamma globulin in the rabbit. The persistence of serum antigens was related to the failure of antibody formation. Renal lesions were not observed following injection of the bovine gamma globulin into irradiated animals, suggesting that antibodies are in some manner related to their development. Hollingsworth (172) has studied the effect of x-rays on the rate of antibody destruction after passive transfer and has determined that there is no difference in the rate of destruction of passively transferred homologous and heterologous antisera given intravenously to rabbits 24 hours after x-irradiation with 300 r. This dosage was sufficient to decrease the formation of antibody to the heterologous serum proteins. While irradiation following immunization with cholera O vaccine does not affect serum

antibody titer, the excretion of fecal and urinary antibody is inhibited (173). With pre-immunization irradiation of the guinea pig, serum antibody titer is reduced but fecal and urinary antibody excretion may show a transitory increase. The latter is seen when immunization is begun at one day, but not three days, after irradiation. This may explain the apparently contradictory findings of beneficial and detrimental effects of irradiation on infection and antibody response.

An interesting aspect of the suppression of antibody formation by total-body x-radiation is the observation by Jacobson *et al.* (174) that the capacity of the irradiated rabbit to produce antibodies to an injected antigen is partially retained if the spleen or appendix is shielded during the exposure. It is not known whether the shielded lymphatic tissue initiates antibody formation or makes it possible for the process to be initiated.

General Physiological Effects

Quantitation of dose-effect relationships has been difficult to achieve for many specific aspects of radiation injury in the mammal. Recently, Carter and his associates (175) have determined that thymic and splenic weights of mice decrease exponentially with increase in radiation dosage over the range of 100 to 1,000 r. The difference in the per cent decrease between a just lethal and almost completely lethal dose is only of the order of 5 per cent, however. The correlation between thymic and splenic atrophy and radiation dosage is seen during the first few days following exposure before appreciable recovery occurs, indicating that linearity may not be observed with extended protraction or fractionation. According to Eschenbrenner & Miller (176) the minimum weight of the mouse testis is also well-correlated with x-ray dosage. The period required for the testis to reach its minimum weight and to return to the pre-irradiation level is likewise a function of dosage. These findings may be useful as biological indices of exposure to a particular radiation and as a means of comparing the various ionizing radiations.

The quantitative aspects of histologic damage to the testes following irradiation have been elaborated upon by several investigators. Eschenbrenner & Miller (176) find that resting spermatogonia, that are present in the mouse testis at the time of x-irradiation, appear to develop normally but that new spermatogonia are not formed. Normal spermatogenesis, in the face of a diminishing number of spermatogonia, has also been seen by Shaver & Mason (177) in the rat during the first two weeks after a total-body exposure to 500 r. Rather similar findings were obtained in mice by Warren, MacMillan & Dixon (178), and in hamsters by Russ (179) after injection of phosphorus-32.

The ocular lesions resulting from radiant energy have been discussed by Cogan (180) who points out that, even though most of the energy incident on the cornea reaches the retina, the latter is relatively radioresistant in contrast to the former. The retina of the young animal is fairly sensitive to radiation, however. Lorenz & Dunn (181) have given newborn mice a total-

body x-ray dose of 400 r and have followed the development of ocular lesions in the survivors. Atrophy of the retina as well as opacities of the lens and cornea were noted in all of the animals alive one year after the irradiation. Von Sallmann (182) observed changes in the periphery of the posterior cortex of the lens within 6 to 14 weeks after local irradiation of the rabbit eye with 2,000 r of 220-kv. x-rays given in single or divided doses. Definite cataracts appeared 11 to 16 weeks after a single dose and 20 weeks after a divided dose. Morphologic changes in the lens cells and irregularities in the staining reaction of the nuclei, suggestive of a decrease in, and depolymerization of, desoxyribonucleic acid, were evident a few weeks after the exposure. On the other hand, Scheie *et al.* (183) report that exposure of the rabbit eye to 2,000 r of soft x-radiation weekly for 5 weeks did not damage the cornea or lens within a $3\frac{1}{2}$-month period. Weekly dosages of 5,000 r for 21 weeks resulted in permanent corneal opacities and cataracts by 14 months after the first exposure. Transient corneal opacities were noted with 500 r given in the same manner. The same authors failed to detect cataract formation in patients whose eyes were given several repeated exposures to 500 r $2\frac{1}{2}$ years previously.

Many of the acute effects of total-body irradiation are referable to injury of the gastro-intestinal tract, which constitutes a sensitive locus for radiation action. In agreement with the earlier observations with x-rays, beta irradiation (P^{32}) of the stomach has been shown by Hedin *et al.* (184) to reduce gastric acidity in the dog and by Douglas *et al.* (185) to result in extensive atrophy of the gastric glands. A transient increase in tonus and in motility of the small intestine of rats has been observed in vitro and in vivo after x-ray doses of 100 r and above (186). Pharmacological and shielding studies suggest that the augmented contraction and rise in tonus are largely a result of a direct effect of radiation on the parasympathetic elements in the intestinal tract. In this regard, synthesis of acetylcholine by brain is enhanced following sublethal x-irradiation (187). This, incidentally, may account for the improved neuromuscular function of hypophysectomized rats with low dose irradiation.

While there is some reason to believe that absorption from the gastro-intestinal tract is impaired following total-body irradiation, Mead, Decker & Bennett (188) point out that in many instances this may be attributed to a change in motility rather than to a direct interference with the mechanism of absorption. In their experiments, mice that received 600 to 700 r x-radiation and were fed a meal of fat at either 2, 24, or 96 hours postirradiation, showed a decreased gastric emptying, increased intestinal motility, and little, if any, impairment of fat absorption. Bennett *et al.* (189) also found little interference in the absorption of vitamin A in rats during the first week following total-body x-radiation with 625 r.

There are few quantitative data that relate to electrolyte changes in irradiated tissues in vivo. No doubt, shifts of water and salts take place in cells that are injured in consequence of irradiation. Painter & Pullman (190) have

determined water and electrolyte changes in the rat intestine following exposure of the total body to x-rays. They observed an increase in sodium that was in part related to an increase in extracellular fluid space and in part due to the exchange of sodium for potassium in the intestinal cells. A similar sodium and potassium exchange has been seen in the irradiated red cell (132).

The acute effects of internal irradiation with radiophosphorus have been studied by Warren and associates (178, 191) and by Grad & Stevens (192). Destructive effects were observed by the former to increase directly with dosage. With an LD_{50} (250 μc. per mouse), maximum injury and recovery occurred sooner in the thymus than in the spleen, bone marrow, and lymph nodes. While diarrhea was severe, it was apparently unrelated to the histologic changes in the intestine. Of interest is their observation that morphologic recovery was accomplished in some animals even though they died later, presumably of radiation injury.

Although it is perhaps reasonable to postulate a significant role for the adrenal gland in resistance to radiation, the evidence remains equivocal. The adrenals do not appear to be peculiarly radiosensitive and are probably involved only secondarily as part of the organism's buffer response to the stress of irradiation. Irradiation has been shown to shorten the life of adrenalectomized rats (193). Cronkite & Chapman (194) note that the 28-day LD_{50} for mice is decreased by approximately 130 r when the animals are adrenalectomized 15 days before irradiation. Actually, these findings do not necessarily conflict with earlier studies in which absolute lethality following a nearly completely lethal dose was not influenced by adrenal insufficiency, for the survival time was shortened under these conditions (195).

Edelmann (193) has reported increased survival in rats whose adrenals are protected with lead shields during the irradiation. On the other hand, recent attempts to counteract radiotoxicity therapeutically with whole adrenal extract, dehydrocorticosterone (196) and cortisone, and ACTH (197) have been unsuccessful. Testosterone, administered to mice daily for the first two weeks following exposure, enhances the lethal effect of x-rays (198). It has been suggested by Ellinger (198) that testosterone augments the adrenal stimulation produced by irradiation. Although some protection is obtained when adrenal cortical extract is given to mice 10 days before irradiation, its administration immediately after the exposure increases mortality in females and is without influence in males (199). Rather similar effects have been observed with estrogens even in the absence of the adrenal glands (200).

Several studies of the effect of exercise on radiation lethality and of the influence of radiation on the performance of exercise have been reported. Kimeldorf *et al.* (201) have observed that the lethality of x-rays for adult rats is increased by repeated vigorous exercise following irradiation. Moreover, the ability of x-rayed rats to perform standardized exhaustive swimming tests is decreased (202, 203). In contrast, Smith & Smith (204) report that irradiation does not decrease significantly the ability of mice to tolerate treadmill running nor does running appreciably increase mortality.

Interest in radiation action even extends to the sphere of sociobiology. The influence of daily exposure to x-rays upon the fighting behavior of mice has been investigated by Vogel (205) who finds that the effects of x-irradiation on trained aggressors are cumulative. Accumulated dosages of 1,200 to 2,000 r were required to eliminate fighting which was, however, not completely suppressed until shortly before death.

Summary

Although it is recognized that the ionizing radiations may act in several ways, depending upon the biological object and the conditions of irradiation, the emphasis in recent work has been directed largely toward the immediate reactions of the aqueous environment. The existence of free radical mechanisms in vivo as well as in vitro is suggested by the rather parallel influence of oxygen and of protective substances on the behavior of aqueous solutions and of living systems to x-rays. However, it is not known whether anaerobiosis and/or protective substances influence all living systems in the same manner. Indeed, there is reason to believe that these factors may, under certain conditions, influence radiosensitivity by altering metabolic pathways within the cell as well as by interfering with radiochemical reactions involving free oxygen and by competing for the products of activated water. Information relating to the relative effectiveness of oxygen and of protective substances for the different qualities of radiation and to their additivity or lack of additivity for a specific radiation quality should aid materially in the elucidation of their mechanism of action.

It is clear that no single change is peculiarly specific for radiation injury. Since the ionizing energy is dissipated in a heterogeneous and highly integrated system, many different effects may ensue and not all of these are a direct consequence of exposure. There are undoubtedly a number of events that contribute to damage and death following irradiation. There is reason to think that chemical effects of ionization and excitation are responsible for the early cytological damage with moderate dosages of radiation and that this, in turn, bears a causal relationship to the over-all injury. Cytological damage apparently leads to deficiencies that are manifest first in areas of rapid cell turnover, the most critical of which are the hematopoietic and intestinal tissues. The essential features of the acute radiation syndrome can be largely explained on this basis. Of significance are the recent observations that morbidity and mortality may be influenced appreciably by procedures that either promote recovery of the blood-forming tissues or prevent bacterial infection.

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RADIOISOTOPES IN BIOCHEMICAL AND MEDICAL RESEARCH[1]

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The tremendous increase in the use of radioisotopes in biochemical research in the past decade has been brought about in part by the obvious advantages of using them in certain types of studies and in part by the greater availability of radioisotopes in general and in particular of relatively large amounts of C^{14}. The general use of isotopes in biochemical research has made it clear that there is no separate "isotope biochemistry" but rather that isotopes are simply tools which are of great importance in attacking certain types of biochemical problems. One of the major contributions to isotope work, one which was the prerequisite for many of the studies, was the development of methods for adapting standard organic syntheses to the microsyntheses of labeled substrates. For example, in January, 1950, some 130 different labeled compounds could be bought from commercial sources; two years before, only C^{14}-methanol was available. Now all sorts of labeled compounds have been prepared—hormones, vitamins, proteins, fats, carbohydrates, and many intermediates in the metabolism of these. Present day work with C^{14}, with its 5,568 year half-life, is quite different from that of the hardy pioneers (1, 2, 38) who worked with C^{11} and had to prepare and purify a substrate, carry on a metabolic experiment, and isolate and determine the radioactivity of the end products before too many of its 20 min. half-lives had passed!

The major use of isotopes in biochemistry has been to elucidate the intimate details of cellular metabolism. Beginning with the classic work of Schoenheimer (3), the concepts of the metabolic pool of the body constituents and the active turnover of cellular materials have become firmly established. Recent work has shown that even such an apparently fixed thing as the calcium of the skeleton (4) is replaced with great rapidity.

Experiments with isotopes have brought to light a number of unexpected facts about cellular metabolism: the existence of a number of carbon dioxide fixing reactions in animal cells in addition to the classic Wood-Werkman one (5), the importance of formic acid and formaldehyde (or a "one-carbon fragment") in intermediary metabolism, the activation of the methyl carbon of acetate (or the "two-carbon fragment") in its condensation with oxalacetate to form citrate, and the fact that chemically symmetrical compounds may behave in metabolism as though they were asymmetrical.

Some idea of the present importance of radioisotopes in biochemical re-

[1] This review is essentially a survey of papers published in 1950.

search can be gained from the fact that of the 300-odd papers presented at the April, 1950, meeting of the American Society of Biological Chemists, 62 were based on work with radioisotopes. At present, although C^{14}, P^{32}, and S^{35} are the most widely used radioisotopes in basic biochemical research, I^{131} is most widely and successfully used clinically. It is used in a diagnostic test for thyroid activity and in the treatment of thyrotoxicosis. P^{32} has found clinical use in the localization of tumors and in the treatment of polycythemia and certain types of leukemia. Until recently, three of the four elements most important biologically, nitrogen, oxygen and hydrogen, have had only heavy isotopes that were practicable for tracer studies. With the development of improved methods for detecting tritium (6), the radioisotope of hydrogen, tracer studies using it have begun.

A review of the uses of radioisotopes in pharmaceutical research was given by Tabern, Taylor & Gleason (7) and recent advances in radiobiology were discussed by Lacassagne (8). The papers presented at a symposium on Radiation Genetics in 1948 were published (9) and provide a review of the newer knowledge in the field; many of the papers are of interest to biochemists.

New Methods in Isotope Research

Crompton & Woodruff (10, 11) have reviewed the chemical methods of synthesizing labeled compounds developed since the publication of "Isotopic Carbon" (12) and Woodruff & Fowler (13) have summarized methods for preparing a total of 83 substances, from glucose to opium, biosynthetically. Current methods of plating, counting, and handling C^{14} in biochemical research have been described by Claycomb, Hutchens, Van Bruggen & Cathey (14); Ingram (15) discussed the hazards and safety measures involved in radiation studies. Robinson (16) described a windowless, proportional flow counter for counting C^{14} that is 12 times as sensitive as conventional end window counters.

A new method of producing radioactive compounds was described by Ball, Solomon & Cooper (17). By placing the amino acid cystine in the atomic pile under the proper conditions of neutron flux, they were able to prepare radioactive cystine and to show, by exhaustive tests and by the preparation of derivatives, that the radioactivity was in the cystine and was due to the conversion in the pile by neutron capture, of S^{34} to S^{35}. The protein hormone, insulin, which is rich in cystine, was made radioactive in a similar fashion (18).

An ingenious method for identifying microgram quantities of amino acids was described by Udenfriend (19, 20) which uses isotopic indicators and paper partition chromatography. The *p*-iodophenyl sulfonyl ("Pipsyl") derivatives of a known amino acid and of the unknown to be tested are prepared, one labeled with I^{131} and the other with S^{35}, and are chromatographed together. If the two derivatives are identical, only one band of radioactivity results and the proportions of the two isotopes are constant throughout the

band. Using this method, γ-aminobutyric acid was identified in protein-free extracts of mouse, rabbit and frog brains (21, 22). It is formed *in vitro* by brain homogenates and its formation is accelerated by the addition of glutamate (22).

The Citric Acid Cycle

An interesting history of the use of isotopes in biochemical research is provided by the citric acid cycle. This cycle of tri- and di-carboxylic acids was postulated by Krebs (23) and has since been shown to be the primary path of oxidation of the products of lipid and amino acid metabolism as well as of glycolysis. Krebs originally suggested that citric acid was an intermediate formed by the condensation of pyruvate and oxaloacetate but early work (1, 24, 25, 26) with isotopes apparently excluded citrate from the cycle, for the distribution of labeling in the resulting α-ketoglutaric acid eliminated the passage of the labeled material through a symmetrical molecule such as citrate. Ogston (27) and Wilcox (28), however, pointed out that if an enzyme formed a three-point connection with its substrate it would be able to distinguish between the two ends of a structurally symmetrical compound. This stimulated a reinvestigation of the question and Potter & Heidelberger (29), isolated symmetrically labeled citric acid from a rat liver homogenate preparation incubation with $C^{14}O_2$. The citric acid was proved to be asymmetric by enzymatic degradation to α-ketoglutarate which was then oxidized to succinate (which had no radioactivity) and carbon dioxide, which had essentially all the radioactivity of the α-ketoglutarate.

Further proof of the validity of the Ogston concept was provided by a number of studies. Wilcox, Heidelberger & Potter (30) synthesized asymmetrically labeled sodium citrate-1-C^{14} from $NaC^{14}N$ and *l*-γ-chloro-β-carboxy-β-hydroxybutyric acid and incubated it with rat liver homogenate. The resulting α-ketoglutarate was isolated and found to contain C^{14} in only the γ-carboxyl group, proof that the asymmetric distribution of isotope in the α-ketoglutarate was derived from the asymmetric distribution of isotope in the citrate and to an antipodal specificity of the enzymes which catalyze the formation and dehydration of citric acid. Lorber, Utter, Rudney & Cook (31, 32) studied the distribution of C^{14} in citrate made by a pigeon liver enzyme preparation from $C^{14}OOH \cdot CH_2 \cdot CO \cdot COOH$ and acetate. By chemical degradation of the citrate they found a significant amount of isotope only in the fractions containing the primary carboxyls, and enzymatic oxidation of the C^{14}-citrate to α-ketoglutarate gave a product labeled exclusively in the α-carboxyl group, indicating that the β-carboxyl of oxaloacetate forms only one of the primary carboxyls of citrate. These workers thus confirmed Potter & Heidelberger's demonstration that labeled citric acid behaves metabolically as an asymmetric molecule. The formation of citrate occurs by an irreversible condensation between the methyl group of acetate and the carbonyl group of oxaloacetate. Yet another confirmation of the Ogston theory came from the experiments of Rudolph & Barron (33) who incubated C^{14}-carboxyl-

labeled acetate and unlabeled oxaloacetate in a rabbit kidney homogenate with magnesium ion, adenosinetriphosphate (ATP), and malonate. The resulting citrate was labeled in the primary carboxyl carbon. The ATP is necessary to render the methyl group of acetic acid labile, presumably by forming an ATP-acetate complex, so that condensation with the carbonyl group of oxaloacetate may occur. The occurrence of this same mechanism in *Aspergillus niger* was demonstrated by Martin, Wilson & Burris (34) who incubated the mold with $C^{14}O_2$, isolated and degraded the citrate formed, and found the isotope exclusively in the carboxyl carbons, almost equally distributed between primary and secondary carboxyls. The presence of C^{14} in the secondary carboxyl group of citrate was presumed to have occurred by a shuttling of oxaloacetate to succinate and back before the condensation with acetate occurred. The citrate producing system of *A. niger* was studied further by Foster, Carson & Jefferson (35) who grew the mold in the presence of C^{14}-methyl-labeled acetate and $C^{13}O_2$ and found, on isolating and degrading the citrate formed, that the distribution of the specific activity of C^{14} and C^{13} in the citrate showed that the four-carbon dicarboxylic acid precursor of citrate can originate by a condensation of two "two-carbon fragments."

Pardee, Heidelberger & Potter (36) showed that rat kidney slices could oxidize C^{14}-carboxyl-labeled acetate only if oxaloacetate was present and concluded that the acetate must condense with oxaloacetate to form citrate in order to be oxidized. α-Ketoglutarate was isolated and shown to contain C^{14}. Tumor tissue was found to have less than one twenty-fifth the activity of kidney tissue. The presence of the citric acid cycle in tumor tissue was demonstrated by Weinhouse, Millington & Wenner (37) who incubated tumor slices with C^{14}-carboxyl-labeled palmitic acid, then isolated quinidine citrate of high specific activity. The palmitate was oxidized at a rate which suggested that fatty acid oxidation may be the prime source of energy of tumors.

Carbon Dioxide Fixation

Something which could have been brought to light only by experiments using isotopes as tracers is the fact that, in animal tissues, carbon dioxide is not merely an inert metabolic product fated solely for excretion, but an active substance which can be incorporated into organic substances. Since the original demonstration of the fixation of carbon dioxide in oxaloacetate by bacteria (5) and animal tissues (2, 24, 38), a number of other reactions in animal tissues have been shown to involve carbon dioxide fixation. Salles and collaborators (39, 40) provide evidence that in pigeon liver preparations the fixation of CO_2 in oxaloacetate is not mediated by a reversal of oxaloacetate decarboxylation (Wood-Werkman reaction) but rather by the triphosphopyridine nucleotide (TPN) dependent "malic" enzyme which fixes the CO_2 in malic acid, after which malic dehydrogenase acts to convert the malate to oxaloacetate. They suggest that the role of ATP in the usual Wood-Werkman

fixation of CO_2 is to supply a source of malic acid from glycogen. The malic enzyme, which catalyzes the reversible oxidative decarboxylation of *l*-malic acid, was isolated, purified, and characterized (41) and its reversibility was demonstrated by $C^{14}O_2$ fixation. The fixation of $C^{14}O_2$ was studied in ox retina and rat diaphragm by Crane & Ball (42) who used pyruvate and $C^{14}O_2$ and isolated pyruvate from the reaction mixture as the 2,4-dinitrophenylhydrazone. They believe that incorporation proceeded via the TPN-dependent malic enzyme, followed by the reversible conversion of malate to symmetrical fumarate, which would result in malate equally labeled in the two carboxyl groups. When this is decarboxylated by the malic enzyme, carboxyl-labeled pyruvic acid results. The question of whether CO_2 is added to pyruvate to give oxaloacetate or malate was considered by Utter (43). Using pigeon liver extracts incubated with $C^{14}O_2$, oxaloacetate, malate, and ATP, he found that the specific activity of the oxaloacetate was three to four times greater than that of malate, but when TPN was used in place of ATP, malate had a specific activity three to four times that of oxaloacetate. Utter concluded that either there are two separate mechanisms, an ATP-dependent system which fixes CO_2 in oxaloacetate and a TPN-dependent one which fixes CO_2 in malate, or there is a single reaction which fixes CO_2 in some intermediate substance following which the intermediate is converted either to oxaloacetate by ATP or to malate by TPN. McManus (44) reinvestigated the process of CO_2 fixation in *Micrococcus lysodeikticus*. In contrast to the pigeon liver enzyme system, the bacterial enzyme is not stimulated by the addition of ATP. It was shown that only oxaloacetate had activity when the products of the reaction were separated by partition chromatography. To test whether the Ochoa "malic" enzyme was present in the bacterial extracts, the fixation of CO_2 in the presence of malate and TPN was measured. No fixation of CO_2 in malate was found, although fixation in oxaloacetate did occur; hence in the bacterial extracts, malate is not an intermediate in the fixation of CO_2 in oxaloacetate.

The practical question of how much $C^{14}O_2$ is fixed by mammalian tissues *in vivo* on chronic exposure was investigated by Buchanan (45) who kept mice in chambers in $C^{14}O_2$ air for periods up to 34 days and found that the total retention of $C^{14}O_2$ was proportional to the $C^{14}O_2$ concentration in the air up to 1.7 per cent. The specific activities of some 30 compounds from the tissues became constant after periods of exposure varying from 1 day for urea carbon to 16 days. From the specific activity/time curve of the erythrocyte carbon it was calculated that the mouse red blood cell life span is 52 days.

Photosynthesis

The long-standing disagreement between the Berkeley and Chicago investigators as to the intermediates in photosynthesis in algae was resolved this year and both groups are agreed that phosphoglyceric acid is the major immediate product in which carbon dioxide is fixed (46, 48). Fager *et al.* (46,

47) confirmed the earlier work of the Berkeley group when they found that phosphoglyceric acid is an intermediate made in response to light and showed that phosphopyruvic acid does not precede phosphoglyceric in the photosynthetic process. The rapid appearance of C^{14} in both the α- and β-carbons of phosphoglyceric acid suggests that the two-carbon acceptor of CO_2 is made by some cyclic process from phosphoglyceric acid; the distribution of tracer, fixed during short periods of photosynthesis, indicates that none of the usual cycles of respiration or fermentation can serve in this cycle for the production of the two-carbon acceptor. Calvin, Bassham & Benson (48) suggest that the two-carbon acceptor is formed by the conversion of phosphoglyceric acid to phosphopyruvic acid, the addition of a second molecule of CO_2 to this to form oxaloacetate and a cleavage of the oxaloacetate to form two two-carbon acceptors of CO_2. The same investigators (49) showed that malate, fumarate, and succinate are not intermediates in the formation of the two-carbon acceptor of CO_2 which is the precursor of phosphoglyceric acid. The Berkeley group concludes (48) that photosynthesis proceeds in two parts: (*a*) the absorption of light energy, its conversion to chemical energy and the use of this chemical energy to decompose water, yielding oxygen and "reducing power"; (*b*) this "reducing power" then converts CO_2 to organic compounds. Experiments with $C^{14}O_2$ showed that the reducing power produced by light has a half-life in the dark of several minutes and that CO_2 fixation can occur in the dark. The experiments suggest that glucose is produced from the phosphoglyceric acid by a reversal of glycolysis. A new challenge to the Berkeley group as to the cycles involved in photosynthesis was made by Steward & Thompson (50), who believe that concurrent protein synthesis is important in the fixation of carbon dioxide.

Aronoff & Vernon (51) found that the primary product of carbon dioxide fixation in soybean leaves is free glyceric acid, in contrast to the phosphoglyceric acid found as the major immediate fixation product in algal cells, and that the second most important fixation product is alanine. Their data, again in contrast to Calvin & Benson's observation that in algae the first free sugar is sucrose, indicated that the first free sugars formed in photosynthesis are the trioses and glucose, followed by sucrose (52). From the distribution of activity in glucose made during short exposures it is clear that the glucose is formed by the condensation of two three-carbon units, two equal halves of nonuniform radioactivity. From a comparison of the radioactivity in the glucose and fructose portions of sucrose, Aronoff & Vernon conclude that the glucose portion is formed before fructose, a conclusion opposite to that derived by Calvin & Benson from their experiments with algae. Vernon & Aronoff (53) then investigated the amino acids formed in short-term photosynthesis and found that alanine had the greatest radioactivity in 15 or 50 sec. exposures, followed by serine and glycine. Both alanine and serine have higher activity in the carboxyl carbon than in C_2 and C_3. The latter two have equal activities. They conclude that alanine is probably involved in the main photosynthetic reaction chain, while serine

and glycine become radioactive indirectly. In contrast to Calvin *et al.*, Aronoff & Vernon believe that the two-carbon CO_2 acceptor does not come from the cleavage of a four-carbon dicarboxylic acid; they were unable to find any radioactivity in any four-carbon dicarboxylic acid in the time periods studied.

Varner & Burrell (54) studying photosynthesis in *Bryophyllum* found that $C^{14}O_2$ was incorporated in the dark as organic acids, chiefly malic; in the light these are converted to starch. When hexoses are made, they are labeled chiefly in carbons 3 and 4, presumably from malate by a reversal of the Wood-Werkman reaction. The labeling of the glucose deposited as starch during photosynthesis in tobacco leaves was studied by Vittorio, Krotkov & Reed (55) who found that after 24 hr. the sugar was uniformly labeled, but that on shorter periods either primarily 3,4- or primarily 1,6-labeled glucose was synthesized, depending on the periods of illumination and darkness used. Wood, Burr & Hartt (56) exposed bean, sugar cane, and rye leaves to $C^{14}O_2$ in the light for short periods of time and analyzed the hexoses made for the distribution of radioactivity. In sugar cane, fixation occurred first in carbons 3 and 4, then in 2 and 5, and finally in carbons 1 and 6. In beans and rye the differences between the carbons were less marked. The great speed of photosynthetic and other cellular enzyme reactions was demonstrated by Clendenning (57) who exposed the alga *Scenedesmus* to light and $C^{14}O_2$ for 40 sec. and found a considerable incorporation of isotope into lipids with approximately equal amounts of C^{14} present in saturated and unsaturated fatty acids.

Carbohydrate Metabolism

The development of methods of preparing C^{14}-labeled glucose in quantity—by the photosynthetic production of starch in a $C^{14}O_2$ atmosphere and the subsequent isolation and hydrolysis of the starch to yield glucose of high specific activity—has made possible many studies of the intermediary metabolism of glucose *in vivo* and *in vitro*. Masoro, Chaikoff, Chernick & Felts (58) showed that the previous nutritional state of the rat had a great effect on the ability of surviving liver slices to convert glucose to fatty acids. Both rats fasted 24 hr. and rats fed a diet devoid of carbohydrate showed a marked reduction in the conversion of glucose to fatty acids by liver slices; it is evident that the presence of carbohydrates in the diet is essential for the maintenance of the capacity of liver tissue to convert glucose to fatty acids. The conversion of glucose to fatty acids is 10 times as great in liver as in kidney slices or diaphragm (59). The size of the body glucose pool, that is, the glucose which is in rapid equilibrium with the glucose undergoing utilization, and its turnover rate was estimated by Feller, Strisower & Chaikoff (60) by injecting C^{14}-glucose intravenously into rats and measuring the specific activity of successive samples of blood glucose. Normal rats have a body glucose pool of 130 mg. per 100 gm. body weight and this turns over at a rate of about 100 mg. per hr. per 100 gm. body weight; about 67 per cent of the glucose is metabolized to CO_2. In alloxan diabetic rats the body pool of

glucose is 260 mg. per 100 gm. body weight and this turns over at a rate of 210 mg. per hr. per 100 gm. body weight but only 27 per cent of the glucose turned over is converted to carbon dioxide. They conclude that although both glucose utilization and the metabolism of glucose to carbon dioxide are reduced in the diabetic rat, the major metabolic defect in diabetes is impaired lipogenesis. This was demonstrated in rat liver slices (61); slices from normal livers convert 0.8 per cent of added C^{14}-glucose to fatty acids, 18 per cent as much as the glucose oxidized to CO_2, whereas slices from diabetic livers failed almost completely to convert glucose to fatty acids. The oxidation of glucose to CO_2 was also markedly depressed in slices from diabetic livers. However, pretreatment of the diabetic rats with insulin for one to five days preceding the experiment brought the ability of the liver slices to convert glucose to fatty acids and to carbon dioxide back to normal (62).

By incubating rat liver slices in C^{14}-glucose and pyruvate-2-C^{14}, Teng, Sinex & Hastings (63) showed that the glycogen formed *in vitro* came almost equally from pyruvate and glucose. Liver from adrenalectomized rats showed an increased ability to synthesize glycogen from both glucose and pyruvate; liver from alloxan-diabetic animals had a decreased ability to form it from glucose but a normal ability to form it from pyruvate. By similar studies with rat diaphragm muscle, Villee, White & Hastings (64) found a decreased ability to form glycogen in both adrenalectomized and in diabetic rats from both glucose and pyruvate. The amount of glycogen made is greater when glucose and pyruvate are present together than from either one alone. In these studies, 75 to 85 per cent of the glucose and pyruvate disappearing from the medium was accounted for as lactate, glycogen, and carbon dioxide produced, proteins and lipids synthesized, and as glucose converted to pyruvate.

A comparison of the metabolism of C^{14}-glucose *in vitro* by tissue slices of heart, brain, kidney, and liver from a variety of mammals and birds, made by Olson, Robson, Richards & Hirsch (65), showed that oxidation of glucose was slow in mammalian liver, 15 to 20 times as fast in heart, kidney, and avian liver, and 60 to 100 times as fast in brain. The rate of oxidation increased as the glucose concentration in the medium increased.

Mosbach & King (66, 67) injected C^{14}-glucose into guinea pigs, gave borneol to stimulate glucuronide formation, and isolated the glucuronide from the urine. By degrading the glucuronide, they were able to show that the carbon chain of glucose is used directly for glucuronide synthesis. Arnstein & Bentley (68) showed that glucose-1-C^{14} is used by *A. oryzae* directly to synthesize kojic acid.

Evidence that mammalian tissues other than the liver can contribute to the blood glucose was supplied by Wick, Drury & MacKay (69), who injected C^{14}-glucose intravenously into eviscerated rabbits, withdrew samples of blood at successive times thereafter, and showed that the blood glucose activity was decreased by the formation of new glucose, presumably by the kidney.

Glucose-1-C^{14}, synthesized from arabinose and $HC^{14}N$ by Koshland & Westheimer (70), was fermented by yeast and the ethanol isolated and degraded. Ninety-five per cent of the activity was found in the methyl carbon of ethanol, confirming present theories of fermentation. A small amount of the radioactivity was found in the CO_2 given off.

C^{14}-labeled glucose has been used to compare the metabolism of normal and cancerous liver tissue. Zamecnik & Stephenson (71) found that hepatoma slices converted glucose to protein 10 to 30 times as fast as normal liver. Hepatoma and normal liver incorporated C^{14} from $C^{14}O_2$ into protein at comparable rates but hepatoma incorporated C^{14} from glucose into protein nine times as rapidly as normal tissue did, which suggests that the two- and three-carbon fragments of glucose are converted to amino acids faster in hepatoma than in normal liver slices. Winzler, Krause & Slater (72), however, found that liver and hepatoma slices metabolize C^{14}-glucose to CO_2 aerobically at comparable rates and that anaerobically hepatoma metabolizes less to CO_2 than liver. The incorporation of isotope into lipids and proteins was much less anaerobically than aerobically.

The fermentation of glucose to lactic acid by *Lactobacillus casei* was shown not to be accompanied by the fixation of carbon dioxide by Gibbs, Dumrose, Bennett & Bubeck (73). With glucose-1-C^{14}, 3 per cent of the activity was in the carboxyl carbon of lactate, and with glucose-3,4-C^{14}, 3 per cent of the activity was in the β-carbon of lactate; they postulate that this randomization of 3 per cent of the activity might be caused by the formation of a symmetrical three-carbon intermediate.

The reactions involved in the synthesis in the intact rat of liver glycogen from fed lactate and propionate doubly labeled with C^{13} and C^{14} were studied by Lorber, Lifson, Wood, Sakami & Shreeve (74, 75). They found, as Topper & Hastings (76) had found in isolated liver slices, that only a small part of the labeled substrate, pyruvate, enters directly into glycogen. Most of it undergoes reactions in the tricarboxylic acid cycle or elsewhere which lead to a randomization of the labeling of the α- and β-carbons of the substrate before it is formed into glycogen by a reversal of the glycolytic reactions. Barnet & Wick (77) showed that the α-carbon of glycine fed to rats is incorporated into glycogen more rapidly than the carboxyl carbon but that the latter is more rapidly converted to CO_2 than the former.

Sodium gluconate uniformly labeled with C^{14} and deuterium was synthesized by Stetten & Stetten (78) and fed to normal and phlorhizinized rats. Much of the gluconic acid was excreted unchanged in the urine but some was oxidized to CO_2 and some was incorporated into the nucleic acids and glycogen of the liver. Since the urinary glucose of the phlorhizinized rat and the liver glycogen of the normal rat were uniformly labeled, a rather direct conversion of gluconate to glucose is indicated.

Chantrenne & Lipmann (79) demonstrated that the exchange of formate with the carboxyl group of pyruvate by *Escherichia coli* is catalyzed by coenzyme A, and postulated that the reaction involves an energy-rich acetyl-

coenzyme A complex formed as an intermediate. Shreeve (80), studying the conversion of lactate-2-C^{14} to acetyl in intact rats and in liver and kidney slices, showed that the kidney is the main site of the acetylating reaction and that the acetyl groups derived from lactate go into acetyls without prior passage through the Krebs cycle. This is in marked contrast to the randomization of three-carbon compounds on their way to liver glycogen (74, 75, 76). Miller & Olson (81), incubating duck heart slices with C^{14}-labeled pyruvate or lactate, found that much more of the substrate disappeared from the medium than could be accounted for by oxidation to CO_2 or by interconversion.

Evidence that four-carbon dicarboxylic acids may arise by a condensation of two two-carbon fragments was derived by Foster & Carson (82) from studies on the biosynthesis of fumaric acid by the mold *Rhizopus nigricans* with labeled CO_2 and ethanol as substrates, and Carson, Foster, Anthony & Phares (83) found evidence from experiments with liver preparations for this mode of origin of the four-carbon dicarboxylic acids.

Roberts (84) showed that *E. coli* cells depleted of potassium had decreased rates of growth and of glucose utilization and incorporated less $S^{35}O_4^{--}$ into protein and less $P^{32}O_4^{---}$ into nucleic acids and phospholipids. She concluded that potassium is involved in one of the early steps of the glucose cycle. Bolton (85) showed that this step is probably at the hexose phosphates, since most of the cellular potassium is present as salts of hexose phosphates.

The interesting observation that C^{14}-carbon monoxide can be metabolized to carbon dioxide by intact mice was made by Clark (86)

Protein Metabolism

Synthesis of proteins.—The nature of the enzymatic reactions involved in the synthesis of proteins has been attacked using both C^{14} and S^{35} as tracers to label amino acids, and, with the synthesis of a variety of these to serve as substrates, these studies have proceeded apace. In some of the early experiments there was some doubt as to whether the tracer was actually present as an integral part of the protein isolated or whether it was adsorbed on the surface. In the more recent experiments it is clear that the tracer is part of the protein but there is some disagreement as to whether its presence there represents "synthesis," "turnover," or "exchange"; many investigators use the word "incorporation" since the exact nature of the process is unknown [Zamecnik & Frantz (87)]. The clearest demonstration so far that a true synthesis of protein may occur *in vitro* with the incorporation of tracer into protein is provided by the work of Peters & Anfinsen (88, 89, 90), who observed an actual increase in the amount of serum albumin present in chick liver slices during incubation in a bicarbonate medium and the incorporation of large amounts of C^{14} from bicarbonate into the carboxyl groups of dicarboxylic amino acids.

Borsook, Deasy, Haagen-Smit, Keighley & Lowy (91, 92) fractionated

guinea pig liver homogenates into four parts by centrifugation and studied the incorporation of C^{14}-labeled glycine, leucine, and lysine into the proteins of these fractions. They found differences in the rates of incorporation and showed that the incorporation of amino acids into protein does not depend on the direct participation of the cell nucleus. The microsome fraction had the greatest rate of incorporation *in vivo* but the least *in vitro* which suggests that the proper experimental conditions for its *in vitro* incubation have not been found. The uptake of the three amino acids incubated together was the sum of the uptake of the three incubated separately. The rate of incorporation of labeled amino acid was not affected by the addition of nonlabeled amino acids to the incubation medium. The independent *in vitro* incorporation of these three amino acids was shown to occur in rabbit bone marrow cells (93) and in rat diaphragm (94). In both of these, the uptake of amino acids was inhibited by anaerobiosis and by inhibitors of oxidation and phosphorylation, which shows that the uptake is a true biochemical process and not simply a physical contamination of the proteins by the labeled amino acid. In both systems, the uptake was a logarithmic function of the initial amino acid concentration up to a certain point, 0.01 *M* for glycine. These three amino acids, plus histidine and L-α-aminoadipic acid, when injected intravenously into mice were found to disappear from the blood within 10 min. (95) and, with the exception of α-aminoadipic acid, which was not incorporated, significant amounts, 18 to 47 per cent of the amino acid injected, were incorporated in visceral proteins within 30 min.

Some of the factors involved in the incorporation of amino acids into protein by cytoplasmic granules obtained by centrifugation from liver homogenates were investigated by Peterson, Greenberg & Winnick (96). The incorporation of C^{14}-labeled glycine, phenylalanine, serine, and methionine was enhanced by ATP, Mg^{++}, citrate, and a mixture of L-amino acids. The uptake of labeled glycine and alanine by homogenates was found by Winnick (97, 98, 99) to be several times greater in fetal or tumor tissue than in normal adult tissue. This incorporation is stimulated by members of the tricarboxylic acid cycle and inhibited by malonate. Evidence that the amino acids are actually incorporated into the protein structure by peptide bonds is provided by the fact that the protein lost no C^{14} when incubated with ninhydrin but lost all its C^{14} when treated with ninhydrin after it had undergone acid hydrolysis.

The synthesis of labeled fibrinogen, plasma albumin, and globulin by intact rat livers perfused with heparinized blood containing lysine-ϵ-C^{14} was shown by Miller, Bly, Watson & Bale (100). Only a small amount of protein was synthesized when only lysine was given but the addition of the essential amino acids increased synthesis tenfold and the addition of the nonessential amino acids increased it still further. D-Lysine was incorporated about 10 per cent as fast as DL-lysine. The addition of glucose increased the synthesis of both liver proteins and the plasma proteins. These investigators (101) showed that tissues other than the liver can synthesize plasma globulin by

perfusing the surviving posterior half of a rat with labeled lysine. The carcass produces much more tissue protein than plasma protein whereas the liver produces roughly equal amounts of tissue and plasma protein. Kelley, Zeigler, Doeden & McQuarrie (102), using S^{35}-labeled methionine, found a higher rate of serum protein formation in nephrotic children than in normal ones, and Kinsell *et al.* (103), studying the rate of incorporation of intravenously injected S^{35}-labeled methionine in the plasma proteins of humans, found a decrease in patients with chronic liver disease. Ethionine, a homologue of methionine, was found to inhibit the incorporation of both methionine and glycine into liver and kidney proteins of intact mice and rats [Simpson, Farber & Tarver (104)]; this inhibition was overcome by the addition of excess methionine.

To prove that the observed uptake of S^{35}-labeled methionine by liver slices is due to the formation of bonds and not to physical adsorption, Simpson & Tarver (105) showed that there was no uptake at 0°C., anaerobically, or in the presence of respiratory poisons. The rate of uptake was found to depend on the concentration of methionine, not on the number of slices. Melchior, Klioze & Klotz (106) incubated *E. coli* with S^{35}-methionine and measured the amount incorporated into proteins. This was increased by the addition of glucose and inhibited by dinitrophenol. Totter, Kelley, Day & Edwards (107, 108) showed that liver homogenates from pteroylglutamic acid (PGA) deficient chicks incorporated less glycine-1-C^{14} into proteins and phospholipids than homogenates from normal chicks. The addition of PGA *in vitro* was without effect. The components of the system which synthesizes peptide bonds in pigeon liver were studied by Johnston & Bloch (109) with the aid of C^{14}-glycine and found to include glutamate, cysteine, glycine, Mg^{++}, phosphate, and ATP or adenylic acid. Peptide synthesis could be caused by amides such as glutamine and asparagine, suggesting that the energy of the amide bond can be used for peptide synthesis. Using carboxyl-labeled acetate and bone marrow slices and homogenates, Abrams, Goldinger & Barron (110) observed an incorporation of the radioactivity into proteins, phospholipids and nucleic acids at a rate paralleling the respiration of the tissue. All of the C^{14} was present in carboxyl groups in the protein, and especially in those of glutamic and aspartic acids. Rutman (111, 112) showed by genetic experiments that two strains of rats differ considerably in the rate at which liver slices incorporate S^{35}-labeled methionine and that part of the difference was due to a factor transmitted from mother to offspring through the milk.

LePage & Heidelberger (113) fed glycine-2-C^{14} to normal and carcinomatous rats, isolated protein, ribonucleic acid, and desoxyribonucleic acid from liver, thymus, and tumor, and found the specific activities of all three higher in tumor than in thymus or liver. In all tissues the rate of incorporation into protein exceeded that into the nucleic acids. Purines and pyrimidines isolated from ribonucleic acid contained C^{14}. A similar study, by Griffin, Bloom, Cunningham, Teresi & Luck (114), in which glycine-2-C^{14} was fed

to rats, however, showed a more rapid incorporation of glycine in normal than in hepatomatous liver in both proteins and nucleoproteins, thus suggesting a metabolic difference between hepatoma and Flexner-Jobling carcinoma. Bucher & Frantz (115) showed by *in vivo* studies that the C^{14}-glycine incorporated into liver proteins can be washed out by the repeated administration of nonlabeled glycine.

The preparation of radioactive crystalline ribonuclease by the *in vitro* incubation of beef pancreas in C^{14}-bicarbonate was described by Anfinsen (116, 117). The synthesis of radioactive ovalbumin by chick oviduct incubated in C^{14}-bicarbonate was described by Villee, Linderstrøm-Lang, Ottesen, Anfinsen & Steinberg (118). The ovalbumin, when acted upon by a *Bacillus subtilis* enzyme, was converted to plakalbumin and three peptides. Aspartic acid isolated from the hydrolyzed peptides had a considerably higher specific activity than the aspartic of the plakalbumin, which suggests that in the synthesis of the ovalbumin molecule the aspartic of the peptide portion enters either from a different metabolic pool or via steps with a different rate from the aspartic of the rest of the molecule.

Amino acid metabolism.—Isotopes have proved to be invaluable in the investigation of the details of the biosyntheses and interconversions of the amino acids. Adelberg & Tatum (119), incubating *Neurospora* with acetate-1-C^{14} or acetate-2-C^{14}, showed that the branched chain of isoleucine is derived from acetate and a four-carbon compound. The synthesis of cysteine by the rat was found by Stekol, Weiss & Weiss (120) to involve the carbons of glycine and the methyl group of methionine. Glycine-2-C^{14} and C^{14}-methyl-labeled methionine were administered and cysteine was isolated from *p*-bromophenylmercapturic acid recovered from the urine. Methionine was shown by Keller, Boissonas & duVigneaud (121) to contribute its methyl group to epinephrine, and by Horner & MacKenzie (122) to be the source of the methyl group of sarcosine. Roberts & Frankel (123) found that mouse brain has an enzyme system which converts C^{14}-glutamic acid to labeled γ-aminobutyric acid, presumably by an α-decarboxylation. Rachele, Reed, Kidwai, Ferger & duVigneaud (124) fed rats S^{35}-labeled L-cystathionine for 23 days and isolated cystine from the fur. From a comparison of the radioactivity of the two compounds it was clear that cystathionine had been the source of the cystine. Using acetate-1-C^{14} and acetate-2-C^{14}, Baddiley, Ehrensvärd, Klein, Reio & Saluste (125) found that the carboxyl carbon of acetate contributes to the carboxyl and ring carbon 4 of tyrosine and the methyl carbon of acetate contributes to the α-, β-, and ring carbons 1, 2, and 6 of tyrosine. The origin of ring carbons 3 and 5 is uncertain. The reversibility of the reactions whereby lysine and tyrosine are decarboxylated was demonstrated by Hanke & Siddiqi (126) who measured the fixation of $C^{14}O_2$ in these amino acids by their decarboxylases.

The biochemical fate of amino acids and their constituent parts was also the subject of studies using radioactive isotopes. Anker (127, 128) showed that L-alanine-2-C^{14} is deaminated to pyruvate, which in turn is converted to

acetate and may be used for acetylating both aromatic and aliphatic amines. D-Alanine-2-C^{14}, in contrast, has some special mechanism, probably a reaction with a keto acid to form an acetyl amino acid, whereby its acetyl group is transferred more rapidly to aliphatic amines. Isovalerate was shown by Coon (129, 130) to be an intermediate in the breakdown of leucine. The C_1 and C_2 of isovalerate form a two-carbon compound which condenses to acetoacetate, and the three carbons of the isopropyl portion are incorporated as a unit into the α, β, and γ-positions of acetoacetate. The carboxyl carbon of this acetoacetate arises from CO_2 by a new type of CO_2-fixation. Thus the complete catabolism of one mole of leucine by the liver gives rise to 1.5 moles of ketone bodies (acetoacetate). Serine labeled in the β-carbon with C^{14} was synthesized by Levine & Tarver (131) and injected into rats. It was incorporated rapidly into tissue proteins and C^{14} was found in ethanolamine, which supports the idea that the pathway of glycine to ethanolamine is by way of serine. Glycine is believed to add formate to give serine and then, by decarboxylation of serine, ethanolamine is formed. Phenylalanine or tyrosine, each labeled in the β-carbon with C^{14}, was injected into phlorizinized rats and the glucose and ketone bodies of the urine were isolated [Sanadi & Greenberg (132)]. From the distribution of radioactivity in the glucose, they conclude that the β-carbons of these amino acids form the methyl carbons of "acetyl" which forms glucose. The amount of C^{14} going to glucose was 50 to 100 per cent of that going to ketone bodies. Similar studies with β-labeled tryptophan (133) showed that only urine glucose became radioactive; no ketone bodies were formed from the β-carbon of tryptophan.

By feeding C^{14}-methyl-labeled methionine to rats and measuring the radioactivity of the expired air, MacKenzie, Rachele, Cross, Chandler & duVigneaud (134) showed that methionine is oxidized *in vivo* in two phases, one of assimilation during the first 7 hr. and one of equilibrium after that. The peak of oxidation occurs at about 3 hr., followed by a decline to about 7 hr., when a low and relatively constant rate is found. Doubling the methionine intake caused a ninefold increase in oxidation during the assimilation period but had little effect on oxidation during the second period. MacKenzie & duVigneaud (135) prepared methyl-labeled creatine and creatinine, fed them to rats, and collected the respired CO_2. This contained little or no C^{14}, thus the methyl group of creatine and creatinine is not oxidized by the intact rat. Meltzer & Sprinson (136) synthesized L-threonine labeled with N^{15} and with C^{14} in the γ-carbon atom and fed it to rats. By isolating acetyl-L-α-amino-γ-phenylbutyric acid and hippuric acid from the urine, they were able to determine that at least 25 per cent of the threonine is converted to acetate and a slightly smaller amount goes to glycine. Almost all the C^{14} of the acetate was in the methyl carbon. In other experiments in which duck blood was incubated with the labeled threonine, and hemin isolated, its C^{14} and N^{15} distributions were in agreement with the known utilization of acetate and glycine for heme synthesis. Ethionine labeled with C^{14} in the methylene carbon of its ethyl group was synthesized and fed to rats [Stekol & Weiss (137)].

Choline isolated subsequently from the tissues had radioactivity only in its trimethyl amine part, which suggests that the de-ethylation of ethionine may occur *in vivo* and that the ethyl portion is available to form ethyl analogues of substances known to participate in transmethylation reactions. Nardi (138) showed that most of the C^{14} administered to mice as glycine is excreted as CO_2 in 48 hr.

Protein metabolism.—A novel method of testing the activity of proteolytic enzymes was devised by Shulman & Tagnon (139) who iodinated fibrinogen with I^{131} and then purified it by dialysis. The fibrinogen was then clotted by thrombin and the resulting fibrin was used as the substrate for proteolytic enzymes, the activity of which was measured by counting the radioactivity set free in the supernatant. The rate of transfer of protein tagged with I^{131} from blood to lymph was measured by Krieger *et al.* (140) and Friedlander *et al.* (141). I^{131}-tagged protein was injected intravenously and samples of lymph were collected from the thoracic duct. Both groups of investigators found that in 2 hr. the specific activity of the lymph protein was about 40 per cent of the plasma protein. Proof that injected cytochrome-*c* is not used by body cells was supplied by Beinert, Matthews & Richey (142, 143), who injected rats with cytochrome-*c* labeled with radioactive iron and found that the cytochrome was either excreted as such by the kidneys or broken down and the iron incorporated into ferritin and red cells. The importance of a high protein diet for the healing of bone fractures was demonstrated by Van Middlesworth (144) who gave rats experimental fractures and incisions and then studied the incorporation of S^{35}-labeled methionine on high and low protein diets. The rats on high protein diets incorporated 10 times as much S^{35} in the fracture callus as in the control, unfractured bone, whereas those on low protein diets showed no localization of S^{35} in the scar.

Porphyrin Metabolism

A considerable advance was made this year in determining the precursors of the carbon atoms of heme and other porphyrin molecules. Wittenberg & Shemin (145, 146), who incubated duck blood with glycine-2-C^{14} and with acetate-1-C^{14} or acetate-2-C^{14}, found that eight carbons of the protoporphyrin molecule come from the α-carbon of glycine: the four methine bridge carbons and the carbons of the pyrrole rings numbered A_2, B_2, C_2 and D_2 by their system—the α-carbon atoms of the pyrroles on the same side as the vinyl and propionic acid side chains. They conclude that in the synthesis of porphyrin, a pyrrole ring is formed which is a common precursor of both types of pyrroles found in protoporphyrin. Most or perhaps all of the rest of the carbon atoms are derived from either the α- or carboxyl carbons of acetate. Radin, Rittenberg & Shemin (147), using glycine labeled with N^{15} and with either its α- or carboxyl carbon labeled with C^{14}, showed that the carboxyl carbon of glycine is not used for heme synthesis. Their data indicate that two α-carbons of glycine are incorporated in heme for each nitrogen atom from glycine incorporated and that glycolic acid, iminoacetic acid,

pyruvic acid, serine, acetic acid, and formic acid are probably not involved as intermediates in the biosynthesis of heme from glycine. Further studies (148) showed that the carboxyl carbon of acetate contributes to the two carboxyl groups present in heme and to at least four of the carbon atoms of the porphyrin ring. The methyl carbon of acetate is converted to the methyl and β-carbon atoms of pyrrole as well as to other, as yet unidentified positions. Muir & Neuberger (149) independently showed that two α-carbons from glycine are incorporated into heme for each nitrogen atom from glycine, that the α-carbon of glycine gives rise to the four methine bridge carbons and to four carbons in the pyrrole rings, and that the methyl carbon of acetate is used to a greater extent in porphyrin synthesis than is the carboxyl carbon of acetate. The α-carbon of acetate was found to be incorporated into the porphyrin ring of chlorophyll at a rate 3.5 times as great as the α-carbon of glycine by Solomon, Altman & DellaRosa (150) who incubated the alga *Chlorella* in the presence of acetate-2-C^{14} or glycine-2-C^{14} for a week and then isolated the chlorophyll. Hubbard & Rimington (151) found that the nitrogen and α-carbon, but not the carboxyl carbon, of glycine are used in the biosynthesis of prodigiosin, the tripyrrylmethene pigment of *B. prodigiosus*, and that both α- and carboxyl carbons of acetate are used and to about the same extent in this biosynthesis. Thus the biosyntheses of prodigiosin and the porphyrin pigments are at least qualitatively quite similar.

The Metabolism of "One-Carbon Fragments"

In the past year or two the importance of "one-carbon fragments," related to formate or formaldehyde, in the metabolism of serine, glycine, and choline has become apparent. Siekevitz & Greenberg (152, 153) showed, using C^{14}-labeled methionine and choline, that the methyl groups of these two compounds can give rise, in liver slices, to formate, which in turn can serve as the source of the β-carbon of serine. This latter reaction is reversible, since the β-carbon of serine can also give rise to formate. Siegel & Lafaye (154) found that C^{14} from formaldehyde is incorporated into the β-carbon of serine faster than the carbon from formate or methanol and hence is a more direct precursor. It also is incorporated more rapidly into the methyl groups of methionine and choline than formate or methanol. These reactions were demonstrated *in vivo* by duVigneaud, Verly & Wilson (155) who injected C^{14}-labeled formate, formaldehyde, or methanol subcutaneously and determined the activity of the methyl groups of choline isolated from the tissues. Large amounts of both formate and formaldehyde are oxidized to CO_2 under these conditions. Matthews & Vennesland (156), using $C^{14}O_2$, showed that the formate dehydrogenase system of green peas is essentially irreversible. Strecker, Wood & Krampitz (157) prepared an enzyme extract from *E. coli* which rapidly fixes formate in the carboxyl group of pyruvate but does not use either synthetic acetyl phosphate or the acid anhydride from pyruvate; they conclude that acetyl phosphate is not a direct intermediate in this fixation of formate. The formation of "biologically labile" methyl groups, those

of methionine and choline, from C^{14}-labeled formate was also demonstrated by Sakami & Welch (158, 159), both in intact rats and in rat liver slices. There was a suggestion in this work that folic acid is concerned with the metabolism of one-carbon compounds such as formate. Sakami (160, 161) administered methyl-labeled acetone to rats and demonstrated the incorporation of the methyl carbon into glycogen, the β-carbon of serine and the labile methyl groups of choline and methionine. This is believed to occur by the oxidation of acetone to a two-carbon and a one-carbon fragment and the subsequent incorporation of the one-carbon fragment into serine and the labile methyls. Plaut, Betheil & Lardy (162) provided further evidence that folic acid but not biotin is involved in the metabolism of one-carbon fragments, for the incorporation of labeled formate into the β-carbon of serine was greater in folic acid fed than in folic acid deficient rats fed C^{14}-formate. There was also a more rapid conversion of formate to CO_2 and to heme in the rats fed folic acid than in those deprived of it. Rat liver slices and homogenates incorporate the carbons of formate and carbonate into the carboxyl carbon of acetoacetate, a process increased by pyruvate but not by acetone or α-ketoglutarate [Plaut & Lardy (163, 164)]. Since formate is rapidly oxidized to CO_2, its incorporation may occur only via carbonate. This is probably the same CO_2-fixation mechanism observed by Coon (129, 130). Carbonyl-labeled acetone was incorporated by rat liver predominantly into the acetone portion of acetoacetate. The fixation of formate and carbonate was much less in biotin-deficient livers than in normal ones. C^{14}-methyl-labeled acetone synthesized by Price & Rittenberg (165), and fed to rats, was shown to be only slowly oxidized; only 50 per cent of the acetone went to CO_2 in 24 hr. Alloxan-diabetic rats are able to oxidize acetone at the normal rate. The acetone is metabolized to acetyl groups and then converted to cholesterol, heme, glycogen, glutamic and aspartic acids, arginine, and to carcass fatty acids. MacKenzie (166) incubated liver homogenates or slices with C^{14}-methyl-labeled sarcosine and demonstrated the formation of formaldehyde, formate, and CO_2. When the radiosarcosine was injected *in vivo*, $C^{14}O_2$ was found in the expelled air and C^{14} formate and formaldehyde in the urine.

The Metabolism of Choline

Choline, betaine, dimethylthetin, and dimethyl-β-propiothetin were each synthesized, labeled with C^{14} in one methyl group, injected into rats, and the amount of C^{14} given off as respiratory CO_2 in 24 hr. measured [Ferger & duVigneaud (167)]. About 12 per cent of the injected choline methyls and about 30 per cent of the methyl carbons of the other three substances were oxidized in 24 hr. Artom & Crowder (168) incubated liver slices with C^{14}-methyl-labeled choline and observed incorporation of C^{14} into phospholipids, trimethylamine, trimethylamine oxide and formate. Using propanediol-1-C^{14}, Rudney (169) observed that the labeled carbon acts in metabolism like the methyl carbon of acetone and goes to the β-carbon of serine, to choline, and

to the 1, 2, 5, and 6 carbons of glycogen and proposed that propanediol is an intermediate, via enol-acetone, in the metabolism of acetone. Since there was some C^{14} in carbons 3 and 4 of glycogen, some propanediol is probably converted to lactic acid, which explains the glycogenic activity of the substance. Burke, Nystrom & Johnson (170) using C^{14}-methyl-labeled methionine, showed the transfer of methyl groups from methionine to choline by intact chicks.

Fatty Acid Metabolism

Pihl & Bloch (171) used acetate-1-C^{14} to study the relative rates of metabolism of neutral fat and phospholipids in various rat tissues. Neutral fats are formed faster than phospholipids in the liver, indicating that phospholipids are not obligatory intermediates in the synthesis of triglycerides. In all other internal organs and in mesenteric fat the isotope concentration in phospholipids was much higher than in neutral fats. Using acetate-1-C^{14}, Pihl, Bloch & Anker (172) determined the rate of turnover or biological half-life of saturated and unsaturated fatty acids and cholesterol in liver and carcass. The rate of turnover of each is much faster in liver than in the carcass and the order is: saturated fatty acids > unsaturated fatty acids > cholesterol. By feeding isovalerate labeled with C^{13} in the methyl groups and C^{14} in the carboxyl group, Zabin & Bloch (173) showed that the isopropyl part of isovalerate goes to acetyl groups and to fatty acids to the same extent as acetate, but is a much more efficient source of carbon for cholesterol. In contrast, the carboxyl part of isovalerate is less efficiently converted to acetyl, fatty acids, or cholesterol than either the isopropyl portion or acetate itself. Fed labeled acetone goes to acetyl, fatty acids, and cholesterol at the same rate as acetate, an indication that acetone is rapidly converted to a two-carbon compound in the body. By incubating liver slices in the doubly labeled acetate (174) they adduced that isovalerate is oxidized at the β-carbon to yield a three-carbon and a two-carbon intermediate and that both of these are metabolized further to acetate. This agrees with the conclusions of Coon (130). The isopropyl portion is more rapidly converted to ketone bodies and less rapidly to CO_2 than is the carboxyl moiety.

Geyer, Shaw & Greep (175) showed that long standing, but not recent, hypophysectomy reduced the rate of utilization and oxidation of C^{14}-octanoate and trilaurin. Hypophysectomized rats had a higher utilization of octanoate compared to its rate of oxidation than normal rats. By incubating carboxyl-labeled pentanoic, hexanoic, heptanoic, octanoic, nonanoic, and dodecanoic acids with liver or kidney slices, Geyer, Cunningham & Pendergast (176, 177, 178) showed the formation of $C^{14}O_2$ and $CH_3 \cdot C^{14}O \cdot CH_2 \cdot C^{14}OOH$. The ratio of acetoacetate to CO_2 is much higher in the liver than in the kidney but the total C^{14} in these products in the two tissues is similar. The ratio of C^{14}-carbonyl-labeled acetoacetate to C^{14} carboxyl-labeled acetoacetate increases as the chain length of the substrate increases and approaches unity for dodecanoic acid. This evidence is against the theory that

acetoacetate is formed by the alternate oxidation and cleavage of fatty acids, and supports the concept of the formation of two-carbon fragments and the condensation of these to give acetoacetate. Geyer, Matthews & Stare (179), incubating carboxyl-labeled octanoate or trilaurin with liver or kidney slices, found that their oxidation to CO_2 was increased by the addition of Krebs cycle intermediates such as fumarate, malate, oxaloacetate, pyruvate and α-ketoglutarate, and decreased by malonate.

Brady & Gurin (180, 181) incubated rat liver slices with C^{14}-labeled acetate, pyruvate, butyrate, hexanoate, and octanoate. All these substrates contributed to long-chain fatty acid synthesis and to cholesterol synthesis. The addition of insulin *in vitro* increased the amount of acetate incorporated into long-chain fatty acids but had no effect on the incorporation of the other substances. Since the long-chain fatty acids made from carboxyl-labeled octanoate are labeled in alternate carbon atoms throughout the molecule, the synthesis of long-chain fatty acids from short-chain ones probably proceeds first by a fragmentation to two-carbon units which are subsequently recombined to form long-chain fatty acids. These investigators then found (182) that liver slices from alloxan diabetic rats or pancreatectomized cats have a greatly reduced ability to convert labeled acetate or octanoate to long-chain fatty acids but have a normal ability to incorporate acetate into cholesterol. The addition of insulin, glucose, oxaloacetate, α-ketoglutarate or fructose-6-phosphate failed to bring fatty acid synthesis back to normal. They demonstrated that diabetic liver is not deficient in fatty acid oxidases nor in acetoacetate nor cholesterol forming enzymes.

Weinman, Chaikoff, Dauben, Gel & Entenman (183) injected palmitate labeled in either the carboxyl carbon, carbon 6 or carbon 11, into rats as the triglyceride and collected the respiratory CO_2. Neither the amount nor the rate of $C^{14}O_2$ production was influenced by the location of the labeling; apparently, once the breakdown process begins, a palmitic acid molecule is disrupted so that all of its carbons are converted to CO_2 at about the same time. When palmitate-1-C^{14} was injected, 11 per cent of the C^{14} was expired as $C^{14}O_2$ in 7 hr. by the normal dog and 4 per cent by the liverless dog (184); thus, less than 40 per cent of the palmitate oxidized to CO_2 in the normal dog was oxidized by all extrahepatic tissues.

Siegel (185) fed $CH_3 \cdot C^{14}H_2 \cdot CH_2 \cdot CH_2 \cdot C^{13}OONa$ and glucose to rats, collected the respiratory CO_2 and analyzed the liver glycogen. He found C^{13} only in carbons 3 and 4 of glycogen and in concentrations too high to be caused by CO_2 fixation alone. C^{14} was found predominantly and equally in carbons 1, 2, 5 and 6. The respiratory CO_2 had twice as much C^{13} as C^{14}; thus the carboxyl and γ-carbons of valerate are metabolized by different pathways. Siegel postulates a β-oxidation to $CH_3 \cdot C^{14}H_2 \cdot COOH$ and $CH_3 \cdot C^{13}OOH$, since the distribution in glycogen was similar to that obtained with carboxyl-labeled acetate and α-labeled propionate. C^{14}-labeled fatty acids made biosynthetically were fed by Coniglio, Anderson & Robinson (186) to fasted rats and the liver and depot fats were studied. In the liver,

the triglyceride fatty acid had more than twice as much C^{14} as the phospholipid fatty acids, confirming the work of Pihl & Bloch (171) whereas the free fatty acids of the liver had the same specific activity as the phospholipid fatty acid. In the depot fat the order of specific activity was: free fatty acids > phospholipid fatty acids > triglyceride fatty acids. Acetate labeled with deuterium and C^{14} was fed to rabbits and the synthesis of cholesterol and fatty acids was followed [Popják & Beeckmans (187)]. They showed that cholesterol is synthesized in the intestine and ovaries, as well as in the liver, but that plasma cholesterol is probably made only in the liver. The synthesis of fatty acids occurred in the intestine and lung as well as in the liver. In the intestine and lung the incorporation of deuterium or C^{14} into phospholipid was faster than the incorporation of isotope into triglyceride; in the liver the two rapidly came into equilibrium. This result is of interest in comparison with the work of Pihl & Bloch (171) and Coniglio, Anderson & Robinson (186).

Yeast cultivated on $C^{13}H_3 \cdot C^{14}OOH$ metabolized two carboxyl groups to CO_2 for every methyl group of acetate; consequently the yeast incorporated more methyl carbon than carboxyl carbon [Baddiley *et al.* (188)]. The carboxyl carbon of acetate was incorporated in yeast mainly as the carboxyl carbon of amino acids. Weinhouse, Millington & Strassman (189) grew yeast on glycine-2-C^{14} and measured the incorporation of C^{14} into lipids. When the lipids were degraded to acetoacetate, the C^{14} was found predominantly in the carboxyl and β-carbons, indicating that the fatty acids had been labeled in alternate carbons. They postulate that glycine adds a one-carbon fragment to form serine, which is then converted to pyruvate, which in turn is metabolized to a two-carbon fragment which condenses to form the fatty acids. Ajl & Kamen (190) incubated *E. coli* with acetate-2-C^{14} and concluded that it does not have a conventional Krebs cycle, since the α-ketoglutarate was not in equilibrium with the four-carbon dicarboxylic acids, but uses primarily a four-carbon dicarboxylic acid system. Barron, Link, Klein & Michel (191) showed that potato slices are able to oxidize carboxyl-labeled acetate or butyrate to $C^{14}O_2$. Stadtman & Barker (192) developed a quantitative method for the chromatography of acyl phosphates of the short chain fatty acids and then showed that the bacterium *Clostridium kluyveri* has enzymes which can transfer phosphoryl groups from acetyl phosphate to fatty acids three to six carbons long.

Bloom, Chaikoff, Reinhardt, Entenman & Dauben (193) fed palmitate-1-C^{14} to rats as the free fatty acid or as tripalmitin. By cannulating the thoracic duct, they were able to recover 70 to 92 per cent of the total fatty acid absorbed in the thoracic duct lymph. Only a small amount of C^{14} was found in the liver; presumably it got there via the portal vein.

Phospholipid Metabolism

Goldman, Chaikoff, Reinhardt, Entenman & Dauben (194) injected palmitate-1-C^{14} intravenously into normal and liverless dogs and measured the

incorporation of labeled fatty acid in the phospholipids of plasma and tissue. Twenty times as much labeled fatty acid was present in the plasma phospholipids of normal as in those of the liverless dogs, indicating that the liver is the principal site of formation of the fatty acid ester bonds of the plasma phospholipid molecules. The liverless dogs incorporated labeled fatty acids into the phospholipids of heart, skeletal muscle, kidney, small intestine, and lung, but since these were not transferred to the plasma, it is suggested that these tissue phospholipids are not normally concerned with the transport of fatty acids from one organ to another. By giving one dog P^{32} inorganic phosphate and tripalmitin labeled with C^{14} in the palmitic acid, Weinman, Chaikoff, Entenman & Dauben (195) produced biosynthetically some plasma phospholipids labeled with both P^{32} and C^{14}. These were then injected into other dogs and the rate of turnover was found to be 0.15 millimole per hr. as measured by the P^{32} and 0.14 millimole per hr. as measured by the C^{14} fatty acids. They conclude that the entire phospholipid molecule is removed as a unit from the blood stream and that there are no exchange reactions which occur either in the blood stream or as the phospholipid molecules pass through the liver.

A lower incorporation of P^{32} into phospholipids by liver slices from rats on low protein diets than by slices from rats on normal diet was shown by Artom & Swanson (196); since the supplementation of the diet with choline did not increase this, the lowered incorporation appears to be due to the lowered protein of the diet and not to a low intake of choline. Cornatzer & Cayer found an acceleration of phospholipid synthesis, as measured by P^{32} incorporation, by methionine or choline in cirrhotic patients (197) but not in normal patients (198). Both growth hormone and adrenocorticotropic hormone (ACTH) were shown by Geschwind, Li & Evans (199) to increase the rate of turnover of liver phospholipids of the rat, as measured by P^{32} incorporation. They also observed a decrease in the uptake of P^{32} by liver phospholipids with age. One of the intermediates in the synthesis of phospholipids by rabbit liver was identified as glycerophosphate by Popják & Muir (200). This synthetic reaction is reversible, for when P^{32}-labeled lecithin or cephalin was injected into rabbits, glycerophosphate isolated from the liver had the highest specific activity. Using P^{32}-labeled phospholipids, Popják & Beeckmans (201) demonstrated that phospholipids injected into a pregnant rabbit are not transmitted through the placenta. There was a decline, as pregnancy proceeded, in the ability of the placenta to absorb and degrade the injected phospholipids.

Steroid Metabolism

Using hepatectomized rats, Srere, Chaikoff, Treitman & Burstein (202) found that a number of tissues other than liver can synthesize cholesterol from C^{14}-labeled acetate: skin, kidney, adrenal, testis, and small intestine. The brain of the newborn, but not adult brain, can synthesize cholesterol. Ottke, Tatum, Zabin & Bloch (203) found that acetate is the preferential

carbon source for ergosterol synthesis in *Neurospora*. When *Neurospora* was grown on isovalerate labeled with C^{13} in the methyl groups and C^{14} in the carboxyl carbon and the ergosterol isolated, it was found that the carbons from the isopropyl portions were a much more efficient source of ergosterol than the carboxyl carbons—further proof that the isopropyl and carboxyl carbons of isovalerate have different metabolic pathways. Little & Bloch (204), using doubly (C^{13} and C^{14}) labeled acetate found that the methyl carbon of acetate contributes to carbons 18, 19, 26, 27 and probably to carbon 17 of cholesterol, whereas the carboxyl carbon of acetate contributes to carbon 25 and probably to carbon 10. Acetate is the principal, if not the sole, source of cholesterol carbons; of the 27 carbons in cholesterol, 15 are derived from acetate methyl carbon and 12 from acetate carboxyl carbon. An equal number of ring and side chain carbons of cholesterol are derived from acetate methyl but more acetate carboxyl carbons are incorporated into the cholesterol ring than into its side chain. Popják & Beeckmans (205) gave C^{14}-labeled acetate to pregnant rabbits and showed that all the fetal cholesterol is synthesized within the body of the fetus; fetal liver can both synthesize and degrade cholesterol but fetal extrahepatic tissues only synthesize it. The synthesis of both saturated and unsaturated fatty acids in fetal liver and extrahepatic tissues was shown to occur.

Grady *et al.* (206) synthesized progesterone-21-C^{14} and injected it into rats. Very little of the activity was found in the expired CO_2; most of it was present in feces, bile, and urine. Estrone sulfate labeled with S^{35} given to adult female rats was found not to be localized in any of the target organs of estrogens in spite of a marked estrogenic response [Davis *et al.* (207)]. Hanahan & Everett (208) found that 75 per cent of the substance given orally, intravenously, or subcutaneously was excreted in the urine and feces in 36 hr. and all of this was excreted as inorganic sulfate. When the labeled estrone was given to rats with a bile fistula, only 15 per cent of the S^{35} appeared in the bile; the rest was excreted in the feces and urine. Liver was the only tissue which could hydrolyze the ester *in vitro*. Dibromestrone labeled with Br^{82} was given to 11 patients, 8 of which had a bile drainage [Twombly & Schoenewalt (209)]. The estrone was found to be excreted primarily via the bile, 39 per cent being excreted by that route, and only 18 per cent via the urine. Those patients with the least liver drainage were found to have the highest rate of excretion. These investigators found that in man as in the rat (207), there is no demonstrable localization of the estrone in either breast or uterine tissue.

Nucleic Acid Metabolism

The rate of turnover of pentosenucleic acid (PNA) in nuclear and cytoplasmic fractions separated by differential centrifugation was studied by Jeener & Szafarz (210) in rat liver, mice embryos, and flagellates, using P^{32} as a tracer. They found that in nonmultiplying cells the highest specific activity was found in the nucleus and that within the cytoplasm the specif-

ic activity decreased from the fractions with the lowest speed of sedimentation to those with the highest speed of sedimentation. They postulate that PNA is synthesized in the nucleus and then passes to the cytoplasm. A higher specific activity in nuclear PNA was also found by Barnum & Huseby (211) who injected P^{32} into mice, isolated the nuclei and three cytoplasmic fractions by differential centrifugation, and determined the specific activity of the phospholipid phosphorus and PNA phosphorus of each of these fractions. The results of these two studies indicate a marked intracellular heterogeneity of PNA. These investigators found a rapid incorporation of P^{32} into the "protein residue" fraction. A similar rapid uptake of P^{32} into the phosphoprotein fraction of adult invertebrate tissues, an uptake much faster than that into the PNA or DNA (desoxypentosenucleic acid), was described by Villee, Lichtenstein, Nathanson & Rolander (212). In contrast, the order of specific activity in embryonic invertebrate tissue is DNA > PNA > phosphoprotein. Adult tissue is characterized by the presence of a considerable amount of DNA which turns over only slowly whereas embryonic tissue has a small amount of DNA which turns over rapidly. A high rate of turnover in the phosphoprotein fraction of normal, pregnancy-stimulated, and cancerous mouse mammary gland was found by Albert, Johnson & Cohan (213). The chemical nature of this phosphoprotein fraction is completely obscure; it is simply what is left after the PNA and DNA have been removed from the acid insoluble phosphorus fraction. Johnson, Albert & Cohan (214) found the highest rate of accumulation of injected P^{32} in the DNA of cancerous mammary glands, the next highest in the DNA of pregnancy-stimulated glands, and the lowest in that of normal ones. The order of accumulation in the PNA fraction was pregnancy > cancerous > normal.

Marshak (215) demonstrated that there are at least two types of nuclei in rat liver, spherical and elongate ones, which can be separated by centrifugation, and which show different rates of P^{32} uptake. Marshak & Vogel (216) injected P^{32} into rabbits intravenously, isolated the liver nuclei by centrifuging, and separated the PNA fraction of the nuclei. By hydrolyzing the PNA, they were able to show that the specific activities of the adenylic acid phosphorus, guanylic acid phosphorus and uridylic and cytidylic acid phosphoruses were approximately equal, which indicates that the component nucleotides of PNA turn over at approximately the same rate.

The synthesis of nucleoprotein but not phospholipid was found to be decreased in the livers of threonine deficient rats [Singal *et al.* (217)]; this could be brought back to normal by giving a single dose of threonine. The incorporation of P^{32} into rabbit spleen, bone marrow, and thymus DNA was shown by Lawrence & Carter (218) to be decreased when nitrogen mustard is injected. The nitrogen mustard also decreased the *in vitro* incorporation of P^{32} by bone marrow cells. The synthesis of PNA and DNA by chick heart cells *in vitro* was found by Hull & Kirk (219) to be very small unless embryo extract was added to the horse serum medium. Kelly & Jones (220) showed that the DNA turnover of mice was decreased when the animals were sub-

jected to total-body irridiation by an injection of colloidal radio-yttrium. A greatly increased turnover of DNA phosphorus in precancerous and cancerous liver tissue from rats given the carcinogenic azo dye *m'*-methyl-*p*-dimethyl aminoazobenzene was reported by Griffin, Cunningham, Brandt & Kupke (221). They found an extremely high rate of incorporation of P^{32} into the nuclear PNA and suggest that this fraction is an intermediary in nucleic acid synthesis (cf. 210, 211). Similar studies in this laboratory had also shown a marked increase in the turnover of DNA phosphorus in precancerous liver from rats treated with the azo dye (222). Kelly & Jones (223) found that the presence of a rapidly dividing tissue mass apparently influences the rate of cell division in other body tissues, for they observed an increase in the DNA turnover of liver, spleen and kidney tissue of mice with mammary gland carcinomas which had not metastasized.

C^{14}-labeled formate was shown by Totter, Volkin & Carter (224) to be incorporated into the nucleotides of DNA and PNA. Skipper, Mitchell & Bennett (225) observed an inhibition of the incorporation of C^{14} from formate and from CO_2 into nucleic acids when aminopterin and aminomethopterin, folic acid antagonists, were given to mice. Mitchell, Skipper & Bennett (226) found an equal rate of incorporation of 8-azaguanine-2-C^{14} into normal viscera and Eo 771 tumor tissue of mice. By isolating and degrading the PNA, the 8-azaguanine was shown to be present in the purines of the PNA. The uptake of C^{14}-adenine into the purine nucleotides of rat nucleic acid was studied by Marrian, Spicer, Balis & Brown (227). Differences in the rate of uptake of P^{32} into DNA by tissues of the gastrointestinal tract were shown by Friedberg (228). Roth, Elliott & Hunter (229) showed that the protozoan *Tetrahymena geleii* has an enzyme capable of splitting phosphate from nucleotides or nucleic acid, for P^{32}-labeled nucleic acids obtained from yeast, when added to the incubation medium, were converted to inorganic phosphate.

Purine and Pyrimidine Metabolism

The biosynthesis of purines and pyrimidines in the rat was studied by Heinrich & Wilson (230) by administering labeled precursors; their results confirmed those of Buchanan, Sonne & Delluva (231) who had used C^{13}-labeled precursors and studied uric acid synthesis in the pigeon: carbon 6 of the purine ring is derived from CO_2, carbon-4 from the carboxyl carbon of glycine, carbon-5 from the α-carbon of glycine, and carbon-2 and carbon-8 from formate. In addition, Heinrich & Wilson observed a new CO_2-fixation mechanism, the fixation of CO_2 into carbon-2 of uracil, a process which occurs at the same rate as the fixation of CO_2 into carbon-6 of guanine. Elwyn & Sprinson (232, 233) synthesized serine labeled with N^{15} and with C^{14} in the β-carbon, fed this to pigeons and isolated uric acid from the excreta. They found that the β-carbon of serine is incorporated into carbon-2 and carbon-8 of uric acid at the same rate as formate. There was some incorporation of the β-carbon of serine into carbon-5 of the ring, probably by a conversion of serine to pyruvate, a randomization of the labeling by a passage through the

Krebs cycle, a reconversion of the pyruvate to serine, and a conversion of the serine to glycine before the incorporation of the glycine into the purine ring at positions 4 and 5. They were unable to confirm the incorporation of the carboxyl carbon of acetate into carbon-2 and carbon-8 of the purine ring claimed by Buchanan, Sonne & Delluva (231) and these latter investigators now believe that their apparent incorporation was due to a contamination of the C^{13}-acetate used with some C^{13}-formate. Edmonds, Delluva & Wilson (234) cultured yeast in C^{14}-formate and found that C^{14} was incorporated into the adenine of nucleotides 10 times faster than into the adenine of nucleic acid. This is in marked contrast to the results of similar experiments with rats, where the two were essentially equal. When yeast was grown on methyl-labeled glycine, an incorporation of C^{14} into the purines but not into uracil was observed.

Greenberg (235), studying the synthesis of hypoxanthine by pigeon liver homogenates, showed that the process involves ammonia, carbon dioxide, glycine, formate, and ribose phosphate and proceeds by way of one or more intermediates and inosinic acid. These studies suggested that 4-amino-5-imidazole carboxamide itself was not involved in the synthesis of purines in this system. However, Miller, Gurin & Wilson (236) synthesized this carboxamide labeled with C^{14}, injected it subcutaneously into rats, and showed an incorporation of the C^{14} in the adenine and guanine of nucleic acid and in the allantoin of urine, and Schulman, Buchanan & Miller (237), incubating this labeled intermediate with pigeon liver homogenates, demonstrated a disappearance of the carboxamide and an incorporation of the radioactivity into hypoxanthine at a rate comparable to that of labeled glycine and formate. Furthermore, when the labeled carboxamide was given to pigeons, C^{14}-uric acid was excreted.

Weed, Edmonds & Wilson (238) synthesized orotic acid-4-C^{14}, incubated it with rat liver slices, and, by separating the purines and pyrimidines by chromatography, demonstrated that C^{14} was incorporated into the pyrimidine acids but not into the purine acids.

Bennett, Skipper, Mitchell & Sugiura (239) prepared 8-azaguanine-2-C^{14}, an analogue of guanine known to inhibit the growth of certain types of tumors, fed it to mice, and found that it is not taken up preferentially by the tumors but is largely excreted in the urine.

Virus Metabolism

Both P^{32} and C^{14} have been used in studies of the process of virus reproduction and of the metabolic relationships between virus and host. Barry, Banks & Koch (240) prepared C^{14}-labeled adenine from *E. coli* grown on $NaHC^{14}O_3$. When this labeled adenine was used as a substrate, the bacteria became labeled in the adenine and guanine of the cellular nucleic acid. When these cells were in turn infected with bacteriophage, almost 50 per cent of the phage purines were derived from the purines of the host cells. Kozloff & Putnam (241, 242, 243) prepared P^{32}-labeled T_6 bacteriophage and used this

to infect bacteria in isotope-free medium under conditions such that only a single generation of bacteriophage was produced. Most of the P^{32} was found in the broth but a significant amount appeared in the virus. When the host cells rather than the virus were labeled with P^{32}, an incorporation of DNA phosphorus from the host into virus DNA phosphorus was observed. They postulated that bacteriophage reproduction involves the independent reproduction of a number of subunits which subsequently recombine to form the final phage particles. When *E. coli* cells were killed by ultraviolet light and placed in a tryptose broth containing P^{32}, a greater uptake of P^{32} was observed when bacteriophage was added [Labaw, Mosley & Wycoff (244)]. It was shown by ultracentirfugation that most of the P^{32} taken up was actually in the phage; the authors conclude that desoxypentose nucleic acid was synthesized from the phosphorus of the medium. Lashbrook & Loring (245) grew tobacco plants in P^{32} and infected them with tobacco mosaic virus; the virus became radioactive. When the radioactive virus was mixed with macerated plant tissue and reisolated, 60 to 90 per cent of the virus was recovered with unaltered radioactivity but when it was inoculated onto growing leaves, only 10 to 20 per cent of the original virus was recovered and over 50 per cent of the radioactivity was found in the supernatant. Thus, during virus duplication the original virus phosphate is largely converted to a nonvirus form.

Winzler, Pearson & Rafelson (246, 247, 248) have studied the growth of mouse encephalomyelitis virus in a minced brain preparation *in vitro* and have found that infected brain has a greater P^{32} uptake than noninfected brain but that the stimulating effect of the virus is ineffective in brain tissue from mice more than seven days old. The growth of virus and the uptake of P^{32} into phospholipid and protein phosphorus fractions were inhibited by lysine, histidine and tryptophan. Benzimidazole, but not 8-azaguanine, inhibited virus propagation and P^{32} uptake into the acid insoluble fractions.

Phosphorus Metabolism

Mazia & Hirshfield (249) showed the importance of the nucleus in the uptake of P^{32} by cutting amebae in two and comparing the uptake of nucleate versus anucleate halves. The nucleate halves took up three to six times as much P^{32} as the anucleate halves. The kinetics of the uptake of P^{32} by the excised mussel gill was studied by Ronkin (250). The uptake of P^{32} by red blood cells was found by Gourley & Gemmill (251) to have the characteristics of a first order reaction, with an activation energy of 16,700 cal., suggesting that the process is a chemical rather than physical one. Further evidence that the uptake of P^{32} by cells is a chemical process was supplied by Popják (252) who found that the process requires energy and is inhibited by sodium azide, known to be an inhibitor of phosphorylation. Mullins (253) found that frog axons took up no P^{32} from the surrounding medium in the presence of azide, in an atmosphere of nitrogen, or at O°C. The Q_{10} for the uptake process is about 2.5.

Bodian & Dziewiatkowski (254) found a higher uptake of P^{32} in the degenerating and regenerating nerves of monkeys than in normal nerve. These investigators (255) injected P^{32} into mice and determined the P^{32} content of inorganic, acid soluble, phospholipid, and protein bound phosphorus in blood and brain. The uptake of P^{32} in the brain was slow, acid soluble phosphorus reaching its peak of activity in 48 hr. and the phospholipid and protein bound phosphorus reaching their peaks only after 120 hr. Causey & Werner (256) injected P^{32} into rabbits, dissected out the nerves, and compared the activities of proximal, middle, and distal portions of the nerves. Nonstimulated nerves had an equal distribution of P^{32} in the three parts but stimulated nerves had a much higher concentration of P^{32} in the direction of the nerve impulse, i.e., decreasing distally in sensory nerves and increasing distally in motor nerves. Lindberg & Ernster (257) injected P^{32} into the subarachnoid space of the brain of the rat and found a rapid turnover—within 2 min., 40 per cent of the phosphate was organically bound, chiefly as ATP and creatine phosphate.

Meyerhof & Green (258, 259) using energy-rich P^{32} compounds showed that intestinal alkaline phosphatase can carry on transphosphorylation from creatine to glycerol and from phosphopyruvic to glycerol or glucose in the absence of nucleotides.

The synthesis of PNA by *E. coli* was found by Abelson & Aldous (260) to be decreased tenfold in the absence of magnesium ions. When rat mammary carcinoma was grown in fertile chick eggs and the system given P^{32}, Galinsky (261) found that the tumor took up more P^{32} than the embryonic brain or liver but the developing chick skeleton took up P^{32} faster than the tumor. Lavik, Harrington & Buckaloo (262) found that a high dose of P^{32}, 4.5 μc. per gm. body weight, administered to rats reduced the amounts of P^{32} taken up by the acid soluble, PNA, and DNA phosphorus fractions as compared to the amounts taken up when a small, tracer dose of isotope was given. Gemzell & Samuels (263) studied the effect of hypophysectomy, adrenalectomy, and corticotropin (ACTH) administration on the phosphorus metabolism of rats. The turnover of inorganic phosphate between cells and extracellular fluid was decreased by hypophysectomy and increased by the injection of ACTH, suggesting that the system which transfers phosphate across cell boundaries is under the control of ACTH. Hertz & Rooney (264) showed an increased uptake of P^{32} by breast or uterine cancer cells when testosterone is administered and Venkataraman, Venkataraman, Schulman & Greenberg (265) reported an increased transfer of P^{32} from plasma to cells in hyperthyroid and a decreased transfer in hypothyroid animals. Thus, thyroxine, testosterone, and ACTH are all implicated in some way in the transfer of phosphate between cells and plasma.

Sulfur Metabolism

A comparison of the rates of fixation of inorganic sulfate labeled with S^{35} by adult and embryonic tissues of the chick was made by Layton (266,

267). The rate of fixation by embryonic tissues was high after 13 to 15 days of incubation and decreased rapidly thereafter until hatching. The conversion of inorganic sulfate to insoluble tissue sulfate was less in adult tissues maintained *in vitro* than in embryonic tissues cultured similarly. The high rate of incorporation of inorganic sulfate during the period of most rapid tissue formation suggests that the sulfate is utilized in the process. Layton found further (268) that regenerating muscle tissue, but not uninjured muscle, grown *in vitro* incorporated S^{35}, presumably as part of the intercellular connective tissue. Further evidence that the formation of new tissue requires the incorporation of sulfate was provided by Cowie & Sands (269), who grew *E. coli* in an S^{35}-sulfate medium and demonstrated that the amount of incorporation was proportional to the number of new cells formed. S^{35}-labeled methionine was identified as one of the products of this incorporation.

Iodine Metabolism

Thyroxine labeled in the 3′ and 5′ positions with I^{131} was given orally or subcutaneously to rats by Clayton, Free, Page, Somers & Woollett (270). They found that the administered material was absorbed from the gastrointestinal tract and excreted in the urine as iodide and in the feces as both organic and inorganic iodine. Gross & Leblond (271) injected small doses of I^{131}-thyroxine and analyzed the organs and excreta afterwards. They found that thyroxine entered all organs tested and was rapidly converted to butanol-insoluble metabolites, but that it was not stored by any organ. Scott & Stone (272) injected rats with I^{131}-labeled iodotyrosines and showed that these substances were secreted by the stomach and reabsorbed lower in the gastrointestinal tract. Animals with tumors had a normal rate of gastric secretion but a reduced rate of intestinal reabsorption, so that they had a higher concentration of iodotyrosines in the gastrointestinal tract.

Meites & Wolterink (273), using I^{131}, found that a primary effect of underfeeding is a reduced thyroid activity. McCullogh, Gold & McKendry (274) found that the rate of uptake of I^{131} in acromegaly is normal or even low in contrast to the high rate in thyroid hypermetabolism. This suggests that the stimulus for the increased rate of metabolism in acromegaly comes from something other than the thyroid. Fitzgerald, Foote & Hill (275), using I^{131} and the methods of radioautography, found that thyroid tumors with abundant colloid collected more iodine than those without colloid. They noted that the concentration of radioiodine in both normal and tumor tissues is extremely uneven so that the calculation of radiation dosage in the tissue is difficult. Stevens, Meinken, Quinlan & Stewart (276) administered NaI^{131} to mice with and without tumors and compared the distribution of the radioiodine in the tissues. Direct measurements of the uptake of I^{131} by normal and pathological thyroids were made by Freedberg, Chamnovitz & Ureles (277), who found that normal thyroids take up 29 per cent of a 150μc. dose in 24 hr., whereas thyrotoxic glands take up 69 per cent and marked hypothyroid glands take up only 8 per cent of the injected dose. The biologic half-life of

I^{131} was found to be 7.5 days in the normal and 5.7 days in the hyperthyroid individual.

By injecting I^{131} and then fractionating the components of a hydrolysate of thyroid tissue by filter paper chromatography, Taurog, Tong & Chaikoff (278) showed that about 15 per cent of the iodine in thyroid is present as monoiodotyrosine, about 20 per cent is diiodotyrosine, and at least 20 per cent, perhaps much more, is present as thyroxine. By similar methods they found that the major radioactive component of the blood is thyroxine and hence that the organic iodine of the plasma is chiefly thyroxine (279). This was found independently by Gross, LeBlond, Franklin & Quastel (280).

Schulman & Keating (281) prepared S^{35}-labeled thiourea and injected it into rats. Ninety-eight per cent of the activity was found in the urine. chiefly as unchanged thiourea, in 48 hours. They observed a 55 per cent concentration of radioactivity in the thyroid. Schulman (282) showed that the labeled thiourea is oxidized by the thyroid to inorganic sulfate and suggested that thiourea prevents the formation of organically bound iodine by saturating the mechanism of the thyroid gland which normally oxidizes the iodide ion. Matthews (283) found that thiouracil given to frogs reduced the uptake of I^{131} to one-fifth that of control animals. Searle, Lawson & Hemmings (284) synthesized a long series of mercaptoglyoxaline derivatives and tested their antithyroid activity by measuring their effect on the uptake of I^{131} by thyroid glands. Wolterink & Lee (285) compared the two methods of determining thyroid activity in rats, by the rate of turnover of radioiodine in the thyroid and by the thiouracil-thyroxine method, and found good agreement; about 5 μg. of D,L-thyroxine are turned over per day per 100 gm. body weight.

Thiocyanate labeled with S^{35} was injected by Wood & Kingsland (286) into rats; those with thyroids deficient in iodine showed no greater uptake of thiocyanate than those with normal thyroids. The rate of uptake of the thiocyanates was about one one-hundredth that of a similar dose of iodide. Rutenberg, Friedman & Seligman (287) prepared nitrogen mustard labeled with I^{131} and compared its uptake with iodide-131 and found that radioactivity accumulated in the thyroid faster when the iodine was administered as nitrogen mustard than when it was given as the iodide. The nitrogen mustard given was rapidly cyclized to the immonium ion with the loss of iodide; but some of the mustard reached and penetrated the cells.

Hamilton, Asling, Garrison, Scott & Axelrod-Heller (288) recommend the use of radioactive element 85, At^{211}, in treating thyrotoxicosis; it induces an extreme degree of radiation injury in the thyroid without injuring the adjacent parathyroids.

The uptake of I^{131} by the brown algae was studied by Kelly (289) who found that it depended on respiration and was increased by added glucose and decreased by added malonate, azide, iodoacetate, and cyanide.

Mineral Metabolism

Neuman *et al.* (4,290) showed that fresh powdered bone suspended

P^{32}-phosphate buffer undergoes a rapid recrystallization. Similar studies showed that the calcium and fluoride of the bone also undergo rapid exchanges, suggesting that even the minerals of the bones of the animal body are in a "dynamic state of equilibrium." The ready exchangeability of the skeletal and plasma calcium *in vivo* was shown by Harrison & Harrison (291) with Ca^{45}. The 50 per cent turnover time of skeletal calcium was found to be 45 hr. in normal rats and 65 hr. in rachitic ones six to eight weeks old. The rate of turnover of skeletal calcium in the pigeon was increased by the injection of folliculin [Dallemagne, Govaerts & Mélon (292)]. Migicovsky & Emslie (293) found, using Ca^{45} as a tracer, that vitamin D affects the rate of absorption of calcium from the gut but not the rate of mineralization in bones. The incorporation of subcutaneously injected Ca^{45} in the milk secreted by a goat was demonstrated by Aten & Heyer (294).

The distribution of injected Co^{60} in tissue of polycythemic rats was studied by Berlin (295), who found that the saturation level is reached rapidly in liver and kidney, more slowly in blood cells and even more slowly in spleen and bone marrow. The metabolism of radioiron in the rat was found by Gubler, Cartwright & Wintrobe (296, 297, 298) to be decreased in infection, and by the injection of turpentine and thorium dioxide.

An increase in the uptake of K^{42} by rabbit white blood cells incubated *in vitro* on the addition of glucose to the medium was reported by Manery *et al.* (299). Roberts & Roberts (300) used K^{42}, P^{32} and S^{35} to study the effects of potassium depletion in *E. coli*. They found that the rates of synthetic processes, growth, and of the incorporation of sulfur into proteins and phosphorus into phospholipids and nucleic acids depend on the amount of bound potassium in the cell. They demonstrated that the phosphorus incorporated into nucleic acids comes primarily from the hexose phosphates. Steward & Millar (301) compared the uptake of Cs^{137} by proliferating and nonproliferating carrot phloem cells. Proliferation was induced by a growth factor from cocoanut milk which increases growth 60 to 80 times. Nonproliferating cells take up ions by the accumulation of salt in the vacuoles whereas the rapidly dividing cells take up and bind cesium in the cytoplasm.

Heath & Liquier-Milward (302) observed that malignant tissues of the mouse take up more Zn^{65} per unit time and weight than comparable normal tissues. The nuclear desoxynucleoprotein from the tumors was found to have an appreciable Zn^{65} content. When labeled zinc phosphate or carbonate was injected intravenously in rabbits [Banks, Tupper & Wormall (303)] half or more of the zinc was found in the lungs in 45 min. and only small amounts in the liver and kidneys; when the zinc was injected as zinc dithizone, 80 per cent of it was found in the lungs. This suggests the formation of colloidal zinc particles which are taken up from the blood stream by the reticuloendothelial cells of the lungs. When carrier-free Be^7 was injected intravenously it was found in the urine and in bone [Scott, Neuman & Allen (304)] but when carrier beryllium was injected simultaneously, Be^7 was recovered in the liver, spleen, and bone marrow, as well as in urine and bone. Presumably the beryl-

lium concentration exceeded its solubility product in body fluids, and particles were formed and taken up by the reticuloendothelial system of these tissues.

An incorporation of injected radioselenium into serum proteins and hemoglobin was observed by McConnell & Cooper (305). Schubert & Wallace (306) found that zirconium or sodium citrate increased the excretion and decreased the retention in tissues of thorium and strontium. Thorium accumulates chiefly in the soft tissues, whereas strontium accumulates mainly in the skeleton. A similar effect of injected zirconium in decreasing the retention of plutonium and yttrium in bone was reported by Schubert & White (307). Schubert, Finkel, White & Hirsch (308) studied the distribution of isotope in blood, liver, and skeleton after the injection of plutonium or yttrium. Both are rapidly removed from the blood; about 45 per cent of the injected plutonium or yttrium was taken up by the skeleton and about half as much by the liver. The data suggest that the controlling factor in the deposition of cations in bone is diffusion.

The Determination of Intra- and Extracellular Volume

Nickerson, Sharpe, Root, Fleming & Gregersen (309) compared several methods of determining blood volume by measuring it simultaneously with T1824 dye, carbon monoxide, and Fe^{55}. By the carbon monoxide method a result 2 per cent larger than with dye and by the radioiron method a result 11 per cent smaller than with dye was obtained. Gray & Sterling (310) described a method of labeling red blood cells *in vitro* with Cr^{51}, and using the labeled cells to determine blood volume. This method is better than the P^{32}-labeling method since there is no exchange of the isotope and has the advantage over the Fe^{55} method of labeling in that the erythrocytes can be labeled *in vitro*. Aikawa (311) used T1824 dye, thiocyanate, and radiosodium to measure fluid volumes in the rabbit; he found that the thiocyanate space was 10 per cent less than the sodium space. Sheatz & Wilde (312) found that intravenously injected S^{34}-sulfate is instantaneously in equilibrium with the sulfate of the red corpuscles of the rat. Their data indicate that sulfate is distributed through 34 per cent of the rat body whereas sodium is distributed through 25.4 per cent of the rat body.

Kaliss & Pressman (313) prepared radioactive iodoproteins (I^{131}) and injected them into mice. By determining the radioactivity of the separate organs they were able to calculate the plasma and blood volumes of the separate organs and the whole mouse. They found the plasma volume to be 6.7 ml. per 100 gm. and the blood volume to be 12.7 ml. per 100 gm. for the whole mouse. The plasma volumes of the separate organs, in ml. per 100 gm. of organs, are: brain, 1.7; kidney, 19.1; liver, 20.2; lung, 23.9; small intestine, 5.0; spleen, 9.2; testis, 3.4. Glucose-C^{14} was injected into normal, eviscerated, and nephrectomized rats by Wick, Drury & MacKay (314) and from the specific activities of successive samples of the plasma glucose they calculated the "glucose space" of the body; this was found to be 31, 26 and 27 per cent of the body weight, respectively, in the three types of animals.

Studies on Permeability

Ten to fifteen years ago, when only such cyclotron-produced radioisotopes as sodium, rubidium, and cesium were available, radioisotopes were used primarily in permeability studies, and a review of the biological uses of isotopes would have had little but these to discuss. Today the study of permeability with the use of isotopes continues but is, perhaps, overshadowed quantitatively by the metabolic studies made possible by the pile-produced isotopes, C^{14}, S^{35}, P^{32} and I^{131}.

Raker, Taylor, Weller & Hastings (315, 316) showed that the potassium ions of human red corpuscles exchange with the plasma potassium at a constant rate, 1.5 millimoles per hr. per l. of cells at 37°C. The temperature coefficient of the exchange reaction proved to be 2.2. It was found that cholinesterase inhibitors decrease the rate of potassium uptake and choline acetylase inhibitors increase the rate at which potassium ions leave the cells.

Jørgensen (317) found that frogs which were depleted of salt by being kept in distilled water for several weeks had an increased rate of uptake of Na^{24} through the skin. They also showed a decreased rate of chloride excretion through the kidney. Lux & Christian (318) studied the permeability of bits of excised frog skin. They found that the iodide-131 ion diffuses through the skin four times as fast as Na^{24}. Grundfest & Nachmansohn (319) exposed excised squid axons to sea water containing Na^{24} and then stimulated the nerves at rates varying from 100 to 300 times per sec. The uptake of sodium by the nerve when stimulated 300 times per sec. was double that under a stimulation of 100 times per sec. When the axons were inactivated by diisopropylfluorophosphonate or eserine, they showed an even larger sodium uptake, which suggests that cholinesterase is associated in some way with a sodium pump. The permeability of the cells of *E. coli* to Rb, Cs, Co, $P^{32}O_4$, $S^{35}O_4$ and S^{35}-sulfide was measured by Roberts & Nieset (320) and found to be rapid. With each isotope, the cells reached a concentration at least 75 per cent of that in the medium within five minutes. About 75 per cent of the cell is "water space" and the ions are freely exchangeable between this water space and the external medium.

Wechsler, Sokoloff & Kety (321) measured the effectiveness of the hepatic circulation by its ability to remove injected Na^{24} from the site of injection. The liver clearance rate is about eight times as fast as the rate for the gastrocnemius muscle. The rate of absorption of subcutaneously injected Na^{24} was found to be increased by the simultaneous injection of hyaluronidase [Forbes *et al.* (322)].

The Synthesis and Application of Isotopically Labeled Drugs

Myers (323) synthesized sulfanilic acid and 2,6-diiodosulfanilic acid labled with S^{35}, diazotized and coupled them to give acidic and basic dyes, and injected the dyes into tumorous mice. He found that the tumors took up the dyes faster than normal tissues but the difference was not great enough to permit the use of these radiodyes in tumor therapy. Sulfapyridine labeled

with S^{35} was synthesized by Bray, Francis, Neale & Thorpe (324) and given to rabbits. They found that there was no significant retention of the drug in tissues after three days nor was there a complete catabolism to inorganic sulfate in this time. They suggest the formation of some intermediate metabolite which cannot be diazotized. Lazarus & Rogers (325) prepared the antihelminthic drug phenothiazine labeled with S^{35} and showed that it was taken up faster by parasite than by host tissue. Penicillin labeled with S^{35} was prepared by Rowley, Cooper, Roberts & Smith (326) and used to determine its site of action in bacteria. The uptake of penicillin by bacteria appears to be a direct chemical reaction with a cellular component present in only minute amounts in resting bacteria but in greatly increased amounts during growth. Simpson & Young (327) synthesized S^{35}-labeled British antilewisite [2,3-dimercaptopropanol (BAL)]. When applied to the skin of rats it was absorbed slowly, distributed through the animal, and excreted in the urine. When injected intramuscularly it was found to leave the muscle within six hours and to be present in almost all tissues. Most of the injected BAL sulfur is excreted in the neutral sulfur fraction of the urine in 24 hrs.

The synthesis of C^{14}-labeled epinephrine was reported by Schayer (328). When this was fed to rats, the majority of the C^{14} was recovered in the urine; some was present in the feces and in the liver, but none was found in the expired CO_2. Adler & Latham (329) showed that codeine labeled with C^{14} in the methoxy group is demethylated by the liver both *in vivo* and *in vitro;* the methoxy carbon is oxidized to CO_2. They were unable to observe any transmethylation *in vitro.* Plotnikoff (330) prepared N-methyl-labeled C^{14}-meperidine and injected it subcutaneously into rats. The expired CO_2 contained 16 per cent of the C^{14} administered, indicating a demethylation of the meperidine. About 10 per cent of the C^{14} was found in the urine and the rest was present in the tissues of the body, there being no preferential concentration of the drug in either the brain or the adrenal gland. Thiopental sodium[5-ethyl-5-(1-methylbutyl)-2-thiobarbiturate; Pentothal] labeled with S^{35} was synthesized by Taylor, Richards & Tabern (331) and injected intraperitoneally into rats. In four days 85 per cent of the S^{35} was excreted in the urine, 23 per cent as inorganic sulfate, 8 per cent as ethereal sulfate, 40 per cent as neutral sulfur, and only 7 per cent as chloroform-extractable sulfur (presumably unchanged thiopental). Thus thiopental is metabolized by the body and a number of degradation intermediates are formed. Lee, Trevoy, Spinks & Jaques (332, 333) synthesized bishydroxycoumarin [3,3′-methylenebis(4-hydroxycoumarin); Dicumarol] labeled with C^{14} in the methylene bridge and injected it intravenously into rats. The activity disappeared rapidly from the blood and was found in liver, bile, and the contents of the intestine. Some 10 per cent was fixed in the liver and remained as long as three days, during which time there was hypoprothrombinemia; thus the period in which bishydroxycoumarin stays in the liver is related to its effectiveness in interfering with the formation of prothrombin.

The carcinogenic substance acetylaminofluorene was synthesized, labeled

with C^{14} in either the acetyl carbon or in carbon 9, and given by stomach tube to rats [Weisburger, Weisburger & Morris (334, 335)]. They showed that the acetyl group is split off from the rest of the molecule and metabolized independently, for it is metabolized to CO_2 but carbon-9 is not. C^{14} could be detected in all the tissues tested but was especially high in the stomach and intestine when either type of labeled dye was fed. Another carcinogenic dye, "butter yellow" (3′-methyl-4-dimethylaminoazobenzene) was synthesized by Salzberg & Griffin (336) and labeled with C^{14} in the ring methyl carbon. When this was fed to rats, no $C^{14}O_2$ appeared in the expired air. The dye was taken up by the liver and other body tissues, and no differences in uptake were observed in rats that had been fed the unlabeled dye for four weeks previously and in control rats.

Schayer (337) synthesized salicylic acid labeled with C^{14} in the carboxyl carbon. When this was administered to rats, most of the radioactivity appeared in the urine within 24 hr. and only an insignificant conversion of the carboxyl carbon to CO_2 was observed. The urine was fractionated and found to contain five radioactive substances; salicylic acid, salicyluric acid, gentisic acid, and two unidentified substances. The plasma contained only salicylic acid and one of the two unidentified substances. Carboxyl-labeled C^{14}-L-ascorbic acid was prepared by Burns, Burch & King (338) and injected into normal and scorbutic guinea pigs; no difference in the incorporation of the ascorbic acid into the tissues could be observed in the two groups. Between 20 and 30 per cent of the injected dose appeared in the respiratory CO_2 in 24 hr. and the urine contained radioactive oxalic acid, demonstrating a conversion of ascorbic to oxalic acid by the body. Jackel, Mosbach, Burns & King (339) studied the synthesis of ascorbic acid in the rat, using chloretone to stimulate synthesis. Approximately 0.3 per cent of administered C^{14}-labeled glucose was converted to ascorbic acid in 24 hr. but only 0.01 per cent of C^{14}-bicarbonate was incorporated into ascorbic acid. When C^{14}-methyl-labeled acetone was given, it was not converted by rat tissues to ascorbic acid nor was it metabolized to CO_2. They calculated that the total transfer of C^{14} from glucose to ascorbic acid in 24 hr. was about equal to the total conversion of dietary carbohydrate to ascorbic acid. This, plus the fact that degradation of the ascorbic acid showed the same ratio of activity in carbons 1 and 2 as in the administered glucose, suggests that in the rat essentially all of the ascorbic acid synthesized comes from glucose.

Beamer, McCollister, Atchison & Spencer (340) exposed the skin of monkeys to $C^{14}Cl_4$ at a level of 1,150 p.p.m. Some of this was taken up by the blood, but it was given off in the expired air rapidly so that skin exposures at this level do not appear to be an industrial health problem. When the labeled carbon tetrachloride was inhaled by the monkeys (341) it was taken up by the depot fat, liver, and bone marrow. Carbon tetrachloride can be metabolized by rat tissue, for some 10 to 20 per cent of the C^{14} in the expired air was $C^{14}O_2$, and the urea of the urine contained some C^{14}.

Chaiet, Rosenblum & Woodbury (342) were able to prepare radioactive vitamin B_{12} by growing *Streptomyces griseus* on CO^{60}.

Radioactive 2,4-dichlorophenoxyacetic acid (2,4-D) was synthesized, labeled with C^{14} in the carboxyl group by Holley, Boyle & Hand (343), and applied to the leaves of bean plants. Some of it was metabolized to $C^{14}O_2$ and excreted, but in five hours more than half of the original material had been converted to a water soluble substance not extractable by ether from an aqueous solution.

The Use of Isotopes in Immunology

Eisen & Pressman (344) prepared rabbit antirat lung and antiovalbumin serum labeled with I^{131}, injected them into rats, and observed the distribution of the radioactivity. The antilung serum showed a specific localization in the lung and in the kidney, evidence that there are some substances in the lung peculiar to it and some found in both lung and kidney. They found, in corroboration of this, that the antilung serum will produce nephritis just as antikidney serum will. Crampton & Haurowitz (345) prepared I^{131}-labeled antigens and injected them into rabbits. When the livers had been homogenized and the homogenates fractionated by centrifuging, they found the highest radioactivity in the mitochondrial fraction and concluded that this fraction is responsible for antibody formation. Dixon, Dammin & Bukantz (346) prepared I^{131}-labeled bovine γ-globulin and injected it into rabbits and mice. Those animals sensitized by previous injections of γ-globulin showed a more rapid decrease of radioactivity in the blood, a more rapid liberation of I^{131} from the protein and a higher level of radioactivity bound to the tissue proteins. When P^{32}-labeled lipovitellin was injected intravenously into rabbits, Banks, Francis, Franklin & Wormall (347) found that more than half of it was localized in the lungs within 2 hr. after the injection and some 10 per cent was localized in the liver. The uptake by lung and liver may have occurred by the incorporation of particulate matter by the reticuloendothelial cells of these two organs. Evidence that the antiserum to lipovitellin has its reactive groups directed towards the phospholipin moiety rather than to the lipoprotein complex as a whole was provided by Francis & Wormall (348) who found that fresh anti-lipovitellin rabbit serum gives precipitates which have significantly higher lipid phosphorus: vitellin phosphorus ratios than the lipovitellin used as the antigen; lipovitellin labeled with P^{32} was used as the antigen.

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STABLE ISOTOPES IN BIOCHEMICAL RESEARCH[1]

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The use of the isotope technique for investigating biological problems has continued at an accelerated rate during 1950. This is partly due to an increased application of the readily available and easily analyzed radioactive isotopes, especially C^{14}. Of greater importance, however, is an increased appreciation of the convenience and versatility of this technique in studying the metabolic pathways of individual atoms of the principle compounds of biochemical significance. Work with stable isotopes has been relatively restricted to investigations involving those elements for which no radioisotope of suitable tracer properties is available. Nitrogen and oxygen are in this category, and hydrogen is a borderline case. The advantages of multiple labeling, usually with a stable isotope and a radioactive isotope in different positions of the same compound, are rapidly gaining recognition. Stable isotopes have generally been preferred in experiments with human subjects.

Natural Abundances

Nier (1) has carried out a carefully designed series of measurements to provide accurate values for the natural abundances of C, N, O, K and A. He calibrated his spectrometers with argon samples of known isotopic composition. These were prepared from pure samples of A^{36} and A^{40} produced by thermal diffusion. The known mixtures were then employed to evaluate the instrumental errors. He finds the natural abundance of N^{15} in atmospheric nitrogen to be 0.365 per cent, of C^{13} to be 1.108 per cent, of K^{39}, K^{40} and K^{41} to be 93.08, 0.0119, and 6.91 per cent, respectively, and of O^{16}, O^{17} and O^{18} of atmospheric oxygen to be 99.759, 0.0374, and 0.2039 per cent, respectively. Becker & Vogell (2) find a value of 0.205_9 per cent for O^{18}, in good agreement with Nier, but their value of 1.12_4 per cent for C^{13} is somewhat higher.

Paleotemperatures

In 1948, Urey (3) developed a method for the determination of the temperatures at which insoluble carbonates were formed. This method is based on the fact that the O^{18} abundance in precipitated carbonates is higher than that of the aqueous medium and is dependent upon temperature. Exact determination of the O^{18} concentration of carbonates of skeletons, either of the present era or of past geologic ages, should yield the temperature of formation. This method depends upon two assumptions: the O^{18} concentration of water has not changed during geologic time, and the O^{18} concentration of

[1] This review is essentially a survey of papers published in 1950.

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the specimen has not changed during the time from its formation to the present.

McCrea (4) has made a careful investigation of this method for the determination of paleotemperatures. He has calculated the fractionation factor for the system calcite-water,

$$\text{fractionation factor} = \frac{O^{18}\ \text{calcite}}{O^{16}\ \text{calcite}} \Big/ \frac{O^{18}\ \text{water}}{O^{16}\ \text{water}},$$

and finds it to change from 1.0254_8 at 0°C. to 1.0205_8 at 25°C. To determine the temperature with a precision of 1° it is necessary to measure the fractionation factor with an accuracy of 0.02 per cent. Such high accuracy is just barely possible at present. Analysis of carbonates slowly formed in the laboratory at temperatures from −1.2° to 79.8° were in excellent agreement with the theoretical calculations. The concentration of O^{18} in the oxygen of carbonates deposited by organisms was usually the same as that of calcium carbonate slowly precipitated from aqueous solution at the same temperature. There are as yet no direct determinations of the O^{18} concentration of the prehistoric oceans, but there is no reason to believe that it was different from the present oceans. It would be interesting in this connection to analyze the water inclusions found in amber. Any changes during the past 10^8 years were certainly small since the greatest part of oxygen of the earth's surface is present as water. Any small change in the ratio of O^{18} to O^{16} in the water would have been accompanied by large changes in that of the sedimentary rocks (3).

The investigations of Urey and McCrea indicate "that such a transient physical quantity as temperature will prove to have been recorded in the rocks in a sufficiently durable form to allow us to read this thermometer at the present time" (3). The further study of the subject, using not only a "carbonate thermometer" but also "phosphate and silicate thermometers" may give us a detailed picture of prehistoric temperature variations on the earth.

One of the unexplained facts concerning the distribution of O^{18} is its enhanced concentration in atmospheric oxygen as compared to water (5). The best determinations show that atmospheric oxygen contains 0.006 per cent higher O^{18} concentration than oxygen from water (6). Dole (7) suggests that this enrichment could result from an exchange reaction between oxygen and carbon dioxide caused by ultraviolet light in the upper atmosphere.

Amino Acids

Schayer (8) has synthesized indole and tryptophan, labeled with N^{15} in the pyrrole rings, and has resolved the tryptophan enantiomorphs. When the labeled indole was administered subcutaneously to rats, a major portion of the compound was excreted in the urine without rupture of the fused rings; no significant conversion of indole to L-tryptophan occurred. Tryptophan experiments confirmed earlier theories that cleavage of the pyrrole ring of

L-tryptophan occurs without removal of the pyrrole nitrogen from its attachment to the benzene ring. Results further support the theory that the resulting kynurenine is oxidized to the α-keto acid which may cyclize to form the substituted quinolines, kynurenic acid, and xanthurenic acid. After injecting rats and rabbits with large doses of L-tryptophan, the kynurenine and the kynurenic and xanthurenic acids were isolated and found to contain only a slightly lower N^{15} concentration than the administered tryptophan. Administration of the natural isomer of kynurenine provided results further substantiating this role of kynurenine. That the ring nitrogen of tryptophan enters the general nitrogen pool was demonstrated by the presence of N^{15} in the ammonia, amino acids, and urea, and the kidney was implicated in the reaction which eventually produces ammonia from the pyrrole ring nitrogen of tryptophan. The labeled pyrrole nitrogen was found not to serve as a significant precursor of heme pyrrole nitrogen. Findings obtained with D-tryptophan indicate that this isomer is oxidatively deaminated to the α-keto acid and reaminated to form L-tryptophan in the rat.

Bonner & Partridge (9) have employed N^{15}-labeled indole (3.97 atom per cent excess) in studies with a double mutant of *Neurospora* which required tryptophan or indole for growth and which accumulated anthranilic acid and quinolinic acid. The anthranilic acid contained no appreciable excess N^{15} and hence was not formed from indole or tryptophan. However, the nitrogen of quinolinic acid was enriched with N^{15} to the extent of 2.98 atom per cent excess. The conclusion is reached that, in *Neurospora*, tryptophan is a major precursor of nicotinic acid, and anthranilic acid is excluded as an intermediate in this nicotinic acid synthesis. Bonner & Wasserman (10), using N^{15}-labeled indole, demonstrated that indole nitrogen is a nicotinic acid precursor in *Neurospora*.

The observation of Mitchell & Nyc (11) that 3-hydroxyanthranilic acid (3-hydroxy-2-aminobenzoic acid) is an intermediate in the metabolic conversion of tryptophan to nicotinic acid has aroused speculation regarding the manner in which a benzene ring bearing an amino substituent can be metabolized to form a pyridine ring (12). Evidence relating to this question has been obtained from the experiments of Leifer *et al.* (13). In their experiments a mutant strain of *Neurospora crassa* which requires 3-hydroxyanthranilic acid for growth was grown in a medium containing unlabeled 3-hydroxyanthranilic acid and $N^{15}H_4Cl$ as the only sources of nitrogen. The N^{15} concentration of the nicotinic acid nitrogen averaged 46 per cent of that in the added $N^{15}H_4Cl$. This finding demonstrated that both ammonium chloride and the amino group of hydroxyanthranilic acid participated in the synthesis of nicotinic acid and further suggested that a symmetrical diamino compound may be an intermediate in the conversion.

The extreme rapidity of conversion of glycine to serine has received further emphasis from experiments wherein glycine-N^{15} was fed to rats and rabbits and the isotope concentrations of tissue glycine and serine nitrogen determined (14). The glycine and serine isolated contained similar concen-

trations of N^{15} demonstrating that the interconversion of these two amino acids is very fast compared with other reversible reactions in which the two amino acids participate. Elwyn & Sprinson (15) investigated the reverse reaction by injecting normal and folic acid deficient rats with L-serine-N^{15} and measured the N^{15} abundance of hippuric acid isolated from urine excreted during the first 24 hr. The N^{15} concentration of the hippuric acid from deficient animals was only one-third that found in control experiments on normal rats. That this difference was not due to an abnormally high glycine turnover in the deficient animals was shown by the results from similar experiments with glycine-N^{15}. Indeed, the glycine turnover in folic acid deficient rats was about one-half of the normal value, as might be expected from impairment of the serine→glycine reaction. This reaction is probably the major endogenous source of unlabeled glycine. A derivative of serine in which the hydroxyl group is replaced by the *p*-aminobenzoyl nitrogen of folic acid is suggested as an intermediate in this reaction.

L-Serine labeled with N^{15} in the amino group and C^{14} in the beta-carbon has been used in a study which shows the labeled atoms to be precursors of the nitrogen and the beta-carbon of choline (16). Glycine-N^{15}-1-C^{14} and glycine-N^{15}-2-C^{14} were also tested as choline precursors and the findings indicate that the amino nitrogen and the alpha-carbon of glycine are first incorporated into serine and that the latter is the source of the ethanolamine portion of choline.

Nakada & Weinhouse (17) have reinvestigated the problem of aspartic acid oxidation by means of experiments wherein L-aspartic acid labeled with C^{13} in the beta-carboxyl position was incubated with kidney and liver slices and liver homogenates. By following the oxygen uptake and the C^{13} concentration of the bicarbonate produced, and by studying the effect of inhibitors and accumulation of products, evidence was obtained that L-aspartate can penetrate liver cells and be oxidized via a transamination with α-ketoglutarate and oxidation of the resultant oxaloacetate by reactions of the Krebs tricarboxylic acid cycle.

The metabolism of L-threonine was studied by Meltzer & Sprinson (18) using L-threonine-N^{15}-4-C^{14}. The relative isotope concentration of excreted hippuric and acetaminophenylbutyric acids and of visceral fatty acids and blood heme provided evidence that a large fraction of the threonine was metabolized by cleavage to acetate and glycine.

Experiments with β-alanine-N^{15} (19) show this alanine isomer to be deaminated by rats at an even faster rate than L-aspartate and glycine. Incorporation of labeled nitrogen into peptide bonds proceeds at the same rate for the three amino acids.

That *Escherichia coli* can synthesize L-tyrosine from some precursor other than L-phenylalanine was shown by the studies of Simmonds (20). A phenylalanine-requiring mutant was cultured in minimal medium containing $N^{15}H_4^+$, and with L-phenylalanine as the only amino acid. The quantity of L-tyrosine synthesized was determined by isotope dilution and by its growth

promoting effect on a tyrosine-requiring mutant; the tyrosine formed was found to exceed the amount theoretically derivable from the added L-phenylalanine. Glucose and ammonia were implicated as the sources of carbon and nitrogen for the tyrosine synthesis. Direct evidence that glucose serves as an immediate precursor of the benzene ring and side chain of phenylalanine and tyrosine has been presented by Gilvarg & Bloch (21). Yeast (*S. cerevisiae*) cultured with glucose-1-C^{14} synthesized phenylalanine and tyrosine of nearly the same high specific activity as the labeled glucose; the isotope was localized in the side chain beta-position and the two and/or six carbon of the benzine ring. When acetate-1-C^{13}-2-C^{14} was used as the test precursor, the relative isotope concentrations of the benzenoid amino acids were much lower. The data indicate that neither acetate nor an intermediate of the tricarboxylic acid cycle derived from acetate could have been immediate precursors. The conversion of acetate to glucose followed by cyclization of the latter would appear to explain the present data as well as those obtained with *Torulopsis utilis* (22).

Fones *et al.* (23) have administered L-valine labeled with C^{13} in the methyl groups to phlorizinized and fasted rats. As much as 38 per cent of the labeled carbon was oxidized to carbon dioxide and exhaled in the respiratory gases; 10 to 12 per cent was converted to glucose in the phlorizinized animal, and a small quantity was excreted as acidic ketone bodies labeled mainly in the carboxyl group. Discussion of the relation of these findings to the mechanism of valine oxidation would appear premature at the present time.

The investigations of the glutamic acid of tumor proteins are continuing at the laboratory of Kögl. Kögl *et al.* (24) have investigated the rate of incorporation of deuterium from the body fluids into the glutamic acid residues of tumor proteins. In four experiments, they isolated a glutamic acid hydrochloride fraction having a rotation about 20 per cent less than that of pure L-glutamic acid hydrochloride. From this fraction they crystallized optically pure L-glutamic acid hydrochloride and a second fraction having an optical rotation close to zero. Deuterium analyses of the L and DL fractions permit the authors to calculate the deuterium concentrations of the D- and the L-glutamic acid hydrochlorides. In three of the four experiments the deuterium concentration of the D isomer was considerably less than the L isomer. The deuterium concentration in the L isomer isolated from the tumor protein was the same as that of the liver protein. Of the five stable carbon-bound hydrogen atoms in the L-glutamic acid of the tumor proteins, three were replaced by deuterium atoms within seven days, while only 0.4, 1.2, 3, and 1.6 atoms were replaced in the D isomer after 7, 12, 17, and 22 days, respectively.

Kögl *et al.* (25) continued the general investigation by feeding DL-deuterioglutamic acid to tumor-bearing rats. In the same manner as in the previous investigation, they determined the isotope concentration in the L and DL fractions of the tumor glutamic acid. In two experiments, they found the deuterium concentration in the L-glutamic acid of liver as well as tumor proteins to be negligible but that in the D isomer to be appreciably higher

than the experimental error. They raised the question whether dietary D-glutamic acid may play a role in tumor physiology. The same authors (26) investigated the metabolism of DL-, D- and L-deuterioglutamic acids after injection in tumor-bearing rats. In all three cases the L-glutamic acid, whether isolated from liver or tumor protein, contained a very low isotope concentration. However after injecting either the DL, or more effectively the D isomer, the deuterium concentration of the D-glutamic acid from the tumor protein was found to possess a considerable deuterium concentration. Such was not the case after injecting L-deuterioglutamic acid.

Trans Reactions

The development of the isotope technique has disclosed the existence of a new class of reactions which were, prior to this, experimentally unobservable. These reactions consist in the substitution of one atom or radical by the same kind of atom or radical. Waelsch *et al.* (27) found an enzyme in a cell-free preparation from *Proteus vulgaris* X19 which catalyzes the exchange of the amide group of glutamine with ammonia:

$$\text{Glutamine} + N^{15}H_3 \rightleftarrows \text{Glutamine-}N^{15} + NH_3.$$

The same preparation catalyzes the reaction of glutamine with hydroxylamine to form γ-glutamohydroxamic acid (28). The authors suggest that the same enzyme is involved in both reactions and that the ammonia and hydroxylamine are substitutes "for other amines of biological significance," i.e., amino acids, and that the enzyme plays a role in peptide synthesis. It is possible to write a series of reactions in which, under the action of this enzyme, the energy of the amide grouping could be used to form an authentic peptide bond (29).

Stumpf (30) finds a similar enzyme system in sugar pumpkin seedlings which catalyzes an exchange reaction between amide-labeled glutamine and ammonia, and Stumpf & Loomis (31) observe that the same system catalyzes the formation of γ-glutamohydroxamic acid from glutamine and hydroxylamine.

Quite similar to these reactions are those reported by Fruton (32) and by Johnston *et al.* (33). They find that benzoylglycinamide and carbobenzoxy-L-methioninamide exchange their amide nitrogen with labeled ammonia under the influence of cysteine-activated papain. They also show that chymotrypsin catalyzes the exchange of the glycinamide moiety of benzoyl-L-tyrosylglycinamide with labeled glycinamide and of the amide group of benzoyl-L-tyrosinamide with labeled ammonia (34). The authors in the above papers discuss the importance of this class of reactions in connection with protein synthesis. Their data clearly demonstrate that the proteolytic enzymes have functional properties other than those which result in the hydrolysis of proteins.

It would appear that in each of the above reactions the same basic mechanism is involved. The enzyme "activates" the amide or peptide link of

RCO-NHX, where X may be H or another group. If water attacks the activated group, hydrolysis of the amide or peptide link results. If ammonia or an amine attacks the activated group, an exchange reaction occurs. If the amino group of an amino acid attacks the activated group, a transpeptidation results. The further study of these important reactions should throw light on the details of the mechanism of action of hydrolytic enzymes and their role in synthetic reactions.

The existence of an enzyme which can hydrolyze a dehydropeptide (35) has raised the possibility that dehydroamino acids are intermediates in amino acid metabolism. Hoberman & Fruton (36) have studied the metabolic fate of N^{15}-labeled acetyldehydrotyrosine. They found it to be metabolically inert; 93 per cent of the N^{15} was excreted within 24 hr. Little of this excreted nitrogen was present in either the ammonia or urea fractions.

Sprinson & Rittenberg (37) synthesized leucine labeled with N^{15} and with deuterium in the alpha, beta, and gamma positions. This quadruply-labeled amino acid was fed to rats, and leucine was subsequently isolated from their proteins. Analysis of this leucine for N^{15} and for deuterium in the alpha, beta, and gamma positions showed that α,β-dehydrogenation had not occurred. On the other hand, a reaction had taken place which had removed the alpha-hydrogen at a rate much faster than the alpha-nitrogen. The same results were observed with α-deuterio-N^{15}-labeled glycine. They suggest that the reversible dehydrogenation of the amino acid to the imino acid is faster than the hydrolysis of the imino acid.

Tanenbaum & Shemin (38) have investigated the scope of the transamination reaction in pig heart employing N^{15}-labeled substrates. Contrary to earlier reports (39), they find extensive transamination between α-ketoglutaric acid and leucine.

Rate of Protein Synthesis

Orekhovich *et al.* (40) and Davydova *et al.* (41) have studied the rate of protein formation in rats by measuring the rate of incorporation of deuterium into proteins from the body fluids. They find the metabolic activity, as measured by deuterium content, to be, in descending order: liver, intestine, spleen, kidney, stomach, heart, lung, and brain. The rate of this reaction is greater in the newborn than in the mother. A group of two-week-old rats fed on mother's milk containing D_2O incorporated deuterium into the proteins of skin and muscle faster than in liver or kidney. The interpretation of these results is complicated by the process of growth superimposed on the dynamic state.

In 1949 Sprinson & Rittenberg (42) presented a method for the determination of the absolute rate of protein synthesis in the intact animal. The method is based on the assumption that the nitrogen of a dietary amino acid is either used for protein synthesis or is excreted. From measurements of the rate of excretion of the nitrogen of an N^{15}-labeled amino acid, they were able to calculate the rate of protein synthesis. Hoberman (43), using a similar

mathematical treatment, has theoretically and experimentally investigated this problem, studying especially the effect of endocrine secretions. Because of the extent of the data and conclusions presented, it is impossible here to adequately review this important paper. In brief, however, Hoberman finds that synthesis is accelerated in adrenalectomized and hypophysectomized rats and that hyperactivity of the adrenal cortex reduces protein synthesis. Protein synthesis is markedly impaired in alloxan diabetes, and the process is only slightly restored by adrenalectomy. He suggests that insulin controls the rate of protein formation by determining the rate of those reactions which supply the energy required for the formation of the peptide bond. Clark (44) has investigated the effect in rats of cortisone on the rate of excretion in urine of the nitrogen of N^{15}-labeled glycine. This hormone results in an increased excretion of the glycine nitrogen. The effect was particularly great in adrenalectomized rats. The data, when evaluated by the method of Sprinson & Rittenberg, indicate that cortisone diminishes the rate of protein synthesis.

White & Parson (45) have studied the rate of excretion in man of N^{15} from labeled glycine and baker's yeast. The excretion rate of N^{15} was slightly slower after feeding yeast than after glycine. The authors suggest that this difference may be partially explained by the fact that the yeast must be digested before absorption. Berenbom & White (46) find that in rats the excretion rates of N^{15} from ammonium-labeled ammonium glutamate and amide-labeled glutamine are approximately equal and twice as rapid as the nitrogen of glycine or L-phenylalanine.

Hoberman & Graff (47) report that when N^{15}-labeled ammonia is fed to rats, the utilization of this nitrogen depends on the supply of glucose in the diet. Starving rats excrete 58 and 71 per cent of the ammonia nitrogen in 10 and 48 hr., respectively; rats on a glucose rich diet excrete but 35 and 46 per cent. Borsook (48), in his review on protein synthesis, has compared the rates of protein synthesis in surviving tissues with values observed in intact animals and finds them to be in better agreement than might be expected.

Nucleic Acids, Purines, and Pyrimidines

The stable isotopes of nitrogen and carbon have been intensively employed in studies on the biosynthesis of nucleic acids from large and presumably more immediate precursors. Brown (49) has reviewed investigations of this type. Schmidt (50) has presented a more general review of recent research on nucleic acids.

It was previously reported that cytosine, uracil, and thymine, the major pyrimidine components of nucleoprotein, cannot be incorporated into nucleotides when administered to animals as free pyrimidines (51, 52). Bendich *et al.* (53) synthesized 2,4-diaminopyrimidine containing excess N^{15} in the 1 and 3 ring positions and the 2-amino group. Although the compound was found to be well absorbed by rats, no significant excess of N^{15} could be detected in liver nucleic acids or in excreted ammonia, urea, or allantoin. Orotic

acid (uracil-4-carboxylic acid) is, however, readily metabolized to form nucleotide pyrimidine. N^{15} from orotic acid is found in both pentosenucleic acid (PNA) and desoxyribosenucleic acid (DNA) (54). A small but significant incorporation of thymine into the DNA of regenerating liver has been reported briefly (49). These findings emphasize a substituent-sensitive enzymatic specificity in the formation of bonds between substituted pyrimidines and D-ribose. The pyrimidines normally found in nucleic acids do not appear to be immediate nucleic acid precursors and hence are probably synthesized after formation of the riboside bond.

Hammarsten, Reichard & Saluste (55) demonstrated that pentose-bound cytosine and uracil are rapidly incorporated into visceral PNA and DNA of rats. The nucleosides administered were prepared by hydrolysis of nucleoprotein from yeast which had been cultured with $N^{15}H_3$. With labeled cytidine (6.93 atom per cent excess) as the test precursor, high isotope concentrations were found in the PNA cytidine (0.463) and uridine (0.385) and the DNA cytosine (0.281), thymine (0.101) and adenine (0.074). Labeled uridine was incorporated into both PNA and DNA to a much lesser extent than cytidine; isolated pyrimidines contained only slightly higher N^{15} concentrations than the purines. These data suggest that cytosine, when linked to ribose or desoxyribose, serves as an immediate precursor of uracil and thymine. The findings are further interpreted as demonstrating the reduction of cytosine-bound D-ribose to D-2-desoxyribose and as indicating that desoxyribose, like ribose (56), is joined to pyrimidines at the 3-nitrogen atom.

The observation of Brown *et al.* (57) that administered adenine can serve as a precursor for both nucleotide adenine and guanine has been followed by investigations on the mechanism of adenine oxidation in the rat. After administration of N^{15}-labeled adenine (0.492 atom per cent excess) at a dosage level of 500 mg. per kg. of body weight, deposits of sparingly soluble 2,8-dioxyadenine (0.473 atom per cent excess N^{15}) were found in the kidneys. From this isotope dilution the endogenous pool of miscible adenine in the rat was calculated to be 20 mg. per kg. of body weight. A possible oxidation intermediate, 2-oxyadenine (isoguanine), was similarly studied, and conversion to 2,8-dioxyadenine occurred. Although no incorporation of N^{15} from isoguanine into the nucleic acid purines could be detected, it was suggested that this compound and 2,6-diaminopurine may still be intermediates in the adenine→guanine reaction when the compounds are attached to ribose. Bendich, Furst & Brown (58) have confirmed previous work (59) demonstrating the use of 2,6-diaminopurine for biosynthesis of nucleotide guanine. When 2,6-diaminopurine labeled with N^{15} in the 1 and 3 positions and the 2-amino group (5.45 atom per cent excess) was administered to partially hepatectomized rats and nucleic acids isolated from the liver, the PNA and DNA guanine were found to contain 0.202 and 0.198 atom per cent excess N^{15} respectively. The PNA guanine synthesis was also demonstrated by the use of 2,6-diaminopurine labeled with C^{13} in the 2 position.

The close relationship which has been established between the heredity-

bearing component of all living cells and desoxyribosenucleoprotein [cf.(49)] has aroused intense interest in the turnover rate of DNA. On the basis of adenine turnover, using N^{15}-adenine as the precursor, Furst, Roll & Brown (60) have calculated the half-time for formation of PNA in normal rat liver to be seven to nine days. The adenine of ribosenucleic acid is thus in a state of dynamic equilibrium comparable to that of liver protein (61). DNA, on the other hand, was formed from adenine at only about 1/100 of this rate; such a slow turnover of DNA was found comparable with the rate to be expected if adenine were incorporated into DNA only during cell mitosis. Partial hepatectomy of the rats resulted in biosynthesis of PNA and DNA from labeled adenine at nearly equivalent rates. This finding was ascribed to increased rate of mitosis under such conditions. Disappearance of PNA N^{15} in the newly synthesized cells proceeded rapidly but the DNA isotope loss was very slow. While these well-co-ordinated studies strongly indicate a "biochemical stability of DNA which helps to furnish the physical permanence, desirable in the gene" (49), investigations with other labeled nucleic acid precursors, phosphate-P^{32} (62), glycine-N^{15} (63, 64), cytidine-N^{15} (55), serine-3-C^{14} (65), and formate-C^{14} (66) imply that some parts of the DNA molecule are in more dynamic states of catabolism and anabolism. A discussion of these apparent anomalies is not appropriate here, but it seems likely on the basis of present information, that there may be more than one precursor for DNA purines and pyrimidines and that biosynthesis can proceed in a manner relatively independent of adenine.

Elwyn & Sprinson (67) have employed both D- and L-serine-N^{15}-3-C^{14} in an investigation of uric acid synthesis in the pigeon. The nitrogen of L-serine was incorporated into position 7 of the uric acid to about the same extent that the beta-carbon entered positions 2 and 8. Utilization of these atoms for the indicated positions was comparable to that of glycine and formate (68) and was ascribable to a rapid formation of these compounds from L-serine [cf. also (14, 15)]. Distribution of N^{15} and C^{14} in the uric acid after injection of D-serine was compatible with the view that this isomer was metabolized via pyruvate and ammonia.

Balance studies and the apparent absence of uricase in human tissues have previously indicated that uric acid is an end-product of purine metabolism in man. The more sensitive isotope technique has sustained the essential veracity of the concept that uric acid is a stable excretion product, although orally-administered uric acid-1,3-N^{15} undergoes substantial conversion to urea-N^{15} (69, 70). However, when the N^{15}-labeled uric acid is injected, very little N^{15} is found in the urea or other nitrogenous components; Benedict *et al.* (71) and Stetten (72) have calculated that uric acid formation exceeds the amount excreted by 20 per cent. Geren, Bendich, Bodansky & Brown (70), using uric acid of lower N^{15} enhancement, found no significant amount of N^{15} in the urea. These workers (70, 71, 72) find the pool of miscible uric acid in normal man to be about 1 gm. and the half life for uric acid turnover is about 0.85 days (70, 71, 72). A number of papers (70, 72, 73, 74)

discuss the enormous increase in the miscible uric acid pool in gouty subjects and the very interesting effect of various therapeutic medications on the above quantities and the uric acid excretion.

Drugs

A method for synthesis of labeled barbiturates has previously been described by van Dyke *et al.* (75); Tabern *et al.* have reviewed the recent studies wherein labeled barbiturates (76) and other drugs (77) were studied with labeled compounds. Maynert & van Dyke (78) administered N^{15}-labeled barbital to dogs and found that this drug, unlike other barbiturates, is not metabolized *in vivo*. Establishment of this fact permitted evaluation of the concentration of barbital in various tissues by merely determining the weight of N^{15} per unit tissue weight. In contrast to previous reports, there was found to be no localized concentration of this compound in a particular division of the central nervous system such as the diencephalon.

The metabolism of pentobarbital has also been investigated (79) with use of anesthetic doses of the N^{15}-labeled compound in dogs. Although about 80 per cent of the N^{15} was excreted within 24 hr., only about 1 per cent appeared as the administered drug and 10 per cent or less as urea. Several theoretical hydrolytic degradation products of pentobarbital were synthesized and used as carriers in unsuccessful efforts to identify the other N^{15} containing excretion products. A large fraction of the N^{15} was coprecipitated with ethyl-(1-methylbutyl)-malonuric acid, but the N^{15}-containing material was shown to be a contaminant by purification of the methyl derivative. Studies with N^{15}-labeled amobarbital (Amytal; ethylisoamylbarbituric acid) (80) gave results similar to those for pentobarbital except that catabolic products of amobarbital are excreted at about one-half the rate of those of pentobarbital. Isotope dilution experiment with ethyisoamylbarbituric acid and the similarly substituted malonuric, acetylurea, and acetamide revealed that these compounds are excreted only in traces. On the basis of further studies with pentobarbital (81), it is suggested that the principal metabolic reaction of the dialkyl barbiturates is a direct oxidative attack on alkyl side chains containing four or more carbon atoms.

Lipids

Anker (82) has studied the *in vivo* acetylation reaction by comparing the acetyl-donating efficiencies of labeled acetate and labeled 3-carbon acetyl donors. It was found that no general differentiation between C_2 and C_3 acetyl precursors can be accomplished by employing the two acetyl-acceptors, aminophenylbutyric acid and *p*-aminobenzoic acid. Four strains of rats utilized pyruvate-2-C^{13} equally well for acetylation of each amine, and acetate is known to be used in a similar manner. The conversions of *dl*-lactic acid-2-C^{14}, pyruvic acid-2-C^{14} and L-alanine-2-C^{14} to labeled acetyl groups were one-fifth to one-half that of acetate, as measured by the relative isotope concentrations of acetylated amines excreted in the urine. However, adminis-

tration of D-alanine, when labeled with either deuterium or carbon-14, resulted in acetylaminophenylbutyric acid with nearly three times the isotope abundance produced from comparable doses of labeled acetate; excreted acetyl-*p*-aminobenzoic acid contained little isotope. These findings are interpreted as being in accord with the theory that only acetate or a closely related C_2 compound acetylates amines *in vivo*, the remarkable acetylating behavior of D-alanine is ascribed to a difference between the kidneys and the liver in the isotope concentration of total acetate available for acetylation.

Studies on the isotope concentrations of cholesterol isolated from rat liver slices after incubation with $C^{14}H_3C^{13}OOH$ and $C^{13}H_3C^{14}OOH$ have been reported by Little & Bloch (83); their findings indicate that 15 of the 27 carbon atoms in cholesterol may be derived from the methyl carbon of acetate, the carboxyl group of the latter supplying carbon for the remaining 12 positions. Degradation studies suggest that five methyl and three carboxyl groups from acetate are used in synthesis of the isooctyl side chain. Methyl groups were identified as sources of carbon atoms 18, 19, 26, 27, and presumably 17. Carbon atom 25 and probably carbon atom 10 are furnished by carboxyl groups of acetate.

Zabin & Bloch (84) have incubated isovaleric acid-1-C^{14}-4,4′-C^{13} with rat liver slices and have determined the isotope concentrations in the resultant acetoacetate and carbon dioxide. The data indicate that isovaleric acid is oxidized at the beta carbon atom to produce C_2 and C_3 intermediates. Both intermediates are subsequently metabolized to acetoacetate and carbon dioxide, complete oxidation proceeding more rapidly for the C_2 unit than the C_3 compound. Further studies (85) by these workers have increased our knowledge on the *in vivo* ketogenic and cholesterol-forming effects of isovaleric acid and its metabolic precursor, leucine. The doubly-labeled isovaleric acid and foreign amines were fed to rats, and acetyl amine was isolated from the urine and cholesterol and fatty acids from the liver. The conversion of the methyl carbon to acetyl groups and fatty acids was similar to that of methyl-labeled acetate but the isopropyl group was much more efficient than acetate as a source of cholesterol carbon. This could indicate that the isopropyl carbon of L-valine is incorporated into positions which are not synthesized from acetate or that the isopropyl group is converted to a cholesterol precursor which can also be formed from acetate. Another plausible explanation is that the labeled valine is preferentially catabolized to acetate in the cells which are most active in cholesterol synthesis, the isotope concentration of acetate being less at the sites of acetylation and fatty acid synthesis. The possibility that the isopropyl group of isovaleric acid is extensively metabolized to cholesterol via acetone was contraindicated by an experiment wherein acetone-1,3-C^{14} and acetate-1-C^{13} were administered simultaneously by stomach tube; the utilization of acetone for synthesis of liver cholesterol was similar to that of acetate. The carboxyl portion of isovalerate was somewhat less efficient as a precursor of cholesterol, fatty acids, and acetyl groups than the other precursors tested.

Popjak & Beeckmans (86) have studied the rate of lipid synthesis in various organs of the rabbit. They injected sufficient D_2O to raise the deuterium concentration of the body fluids to a level of 1.5 per cent and supplied drinking water containing 2 per cent D_2O to maintain the deuterium level *in vivo* at about 1.5 per cent deuterium. Simultaneously carboxyl-labeled C^{14} acetate was administered. The authors found the incorporation of deuterium into the intestinal cholesterol to be more rapid than in the liver cholesterol. Similarly, C^{14} is more rapidly incorporated in the cholesterol of the intestine and ovary than into the liver cholesterol. The same rapid incorporation of deuterium and C^{14} into intestinal glyceride fatty acids and phospholipid fatty acids in comparison to the liver lipids was observed. Especially striking results were obtained in comparison of C^{14} activity of the lung and liver phospholipid fatty acids. The former were from 30 to 45 times as radioactive as the latter. The amount of data in this paper makes it difficult to give an adequate summary in a brief review.

The authors refer to the finding of a higher deuterium concentration in the intestinal cholesterol than liver cholesterol as "proof of an extrahepatic synthesis." The reviewers are not convinced that such evidence constitutes proof. The authors would be correct if the indicated organs were chemically homogeneous. In fact, such is not the case, and it is at least possible that the lipids in any organ are a mixture of metabolically active as well as of relatively inactive material. Such is known to be the case for proteins (61). If such mixtures actually are present, then it would be possible for the isotope concentration of the lipids of one organ to have a higher isotope concentration than the liver lipids even though all the lipids were synthesized in the liver. It would merely require that the liver contain more metabolically inert lipids than the other organ. It is unlikely, however, that this objection can account for the enormous differences between the isotope concentrations in the lung and liver fatty acids. Another difficulty arises in the interpretation of the data from such experiments if the diet is not lipid-free since these lipids may be deposited in various amounts in the various organs. It is known from experiments in which labeled fatty acids are administered that proportionately more of them are deposited in the liver than in most other organs. If the diet in these experiments were not free of fats, these fatty acids would depress the isotope concentration in the lipids of the liver more than in some other organs. In this regard it is noteworthy that when Bloch, Berg & Rittenberg (87) fed deuteriocholesterol to a dog the highest deuterium concentration was found in the cholesterol isolated from the lungs.

The use of D_2O to study the relative rates of deposition of new cholesterol in various organs has also been reported by Alfin-Slater *et al.* (88); their results suggest that the adrenal glands, lungs, and liver are the most active tissues in cholesterol synthesis. Recent findings of Srere *et al.* (89) with functionally hepatectomized rats leave little doubt that cholesterol synthesis occurs in many tissues.

The observation that biotin deficiency is accompanied by an elevated level of serum cholesterol (90) has raised the question of whether this condi-

tion is characterized by an increased rate of cholesterol synthesis. Curran (91), using deuterium uptake as a criterion of the rate of cholesterol synthesis, found that the rate is not increased in biotin deficiency. Liver and carcass deuteriocholesterol were formed from heavy water at the same rate in deficient and normal rats. A detectable increase in the rate of fatty acid synthesis was observed, but this was attributable to the inanition (92) accompanying biotin deficiency and not to the deficiency itself.

The development of the isotope technique is gradually producing kinetic data on the rate of formation of tissue constituents. In the mathematical treatment of these data, the assumption is generally made that the reaction is first order. Such is not always the case. Shemin & Rittenberg, in their study on the life span of the human red cell (93), found that the Volterra integral equation of the second type was needed to analyze their data. The application of this equation to the analysis of kinetic data from experiments using labeled molecules has been generalized by Branson (94). This method of mathematical analysis should find wide use.

Ottke *et al.* (95) studied the biosynthesis of ergosterol in nonspecific and acetate-requiring strains of *Neurospora*. In experiments with heavy water and deuterioacetate as test precursors, strong evidence was obtained that essentially all of the hydrogen in ergosterol synthesis may be supplied by acetate (24.4 per cent) and water (69 per cent). A C_2 compound derived from or identical with acetate and more remote from ethanol is implicated as an essential precursor of ergosterol; however, a maximum of about 30 per cent of the acetate-derived hydrogen can apparently be supplied by an unidentified nonacetate catabolic product of sucrose. That a hexose from sucrose is not a direct precursor of the 6-carbon rings of ergosterol is shown by an experiment on the wild strain of *Neurospora* which can produce the carbon precursors of ergosterol from sucrose. The process is accompanied by replacement of all the sucrose hydrogen atoms by hydrogen from water. The infrared spectra of ergosterol isolated from *Neurospora* grown on deuterioacetate and on normal acetate in D_2O show distinct and different peaks, especially in the region of the carbon-deuterium bond-stretching frequencies, showing that the location of deuterium in the sterol molecule differs in the two cases. The biosynthesis of ergosterol in this mold is strikingly similar to cholesterol formation in rats.

The metabolism of acetate in *Torulopsis utilis* has been studied with $C^{13}H_3C^{14}OOH$ (96). When the acetate-adapted yeast was grown on labeled acetate as a sole carbon source, the isotope concentrations of respiratory carbon dioxide showed the carboxyl groups of acetate to be oxidized twice as fast as the methyl groups. The carboxyl carbon was utilized to a lesser extent for tissue synthesis; it was found to be mainly in the carboxyl position of amino acids but was also present in noncarboxylic parts of some neutral and basic amino acids. Tyrosine was isolated and degraded in an attempt to elucidate the biosynthesis of benzene rings (22). Carbon atoms in the adjoining alpha, beta, and 1 positions contained 0.25 to 0.26 atom per cent excess C^{13}, and the average concentration of carbons 2 and 6 was 0.26 per cent.

Carbons 3 and 5 possessed an average C^{13} enrichment of 0.135 per cent, and carbon 4 had only 0.005 per cent. The C^{14} was localized in the 4 and carboxyl positions. The authors observe that such an isotope distribution would be expected from an acetate plus oxaloacetate type of condensation rather than the head-tail acetate condensation employed in sterol synthesis. Other workers (21) have extended this reasoning to point out that the distribution mentioned above would be expected if the acetate entered the benzene ring via glucose as shown by their own results.

Cutinelli, Ehrensvärd & Reio (97) have conducted investigations similar to the above except that anaerobic conditions were maintained. *Rhodospirillum rubrum* will grow without air when exposed to light and acetate and bicarbonate suffice as sources of carbon. Suitable parallel incubations with $C^{13}H_3C^{14}OOH$ and $NaHC^{14}O_3$ provided bicarbonate and protein isotope distributions quite similar to those obtained aerobically with *Torulopsis utilis*. Forty-five per cent of the total protein carbon was derived from the methyl group of acetate, about 23 per cent from the acetate carboxyl group, and 10 per cent from the bicarbonate pool of the medium.

Strecker, Wood & Krampitz (98) have employed an aqueous extract of *E. coli* in studies on the fixation of labeled formate into the carboxyl position of pyruvate. Although the preparations were very active in such fixation, the simultaneous presence of acetyl phosphate-1-C^{13} and acetate-2-C^{13} did not produce C^{13}-labeled pyruvate. Acetyl phosphate is therefore not a direct intermediate in the fixation of formate in pyruvate. Aged preparations of the enzyme system lost the ability to catabolize pyruvate yet retained their original activity for fixation of labeled formate. Further studies with *Staphylococcus aureus* showed this organism to fix formate in the carboxyl position of pyruvate even though it does not produce an appreciable amount of formate. These findings indicate that there is no correlation between the extent of the formate-producing phosphoroclastic reaction and formate fixation. One of the possible explanations advanced to explain the data involves an exchange reaction as follows:

$$CH_3{\cdot}CO{\cdot}COOH + HC^{*}OOH \longrightarrow \left[CH_3{\cdot}C(C^{*}OOH)(OH){\cdot}COOH\right] \longrightarrow CH_3{\cdot}CO{\cdot}C^{*}OOH + HCOOH$$

The existence of such exchange reactions in biological systems, if confirmed, would introduce a complication in the interpretation of data involving isotope concentrations of formate, α-keto carboxyl groups, and their equilibrium products.

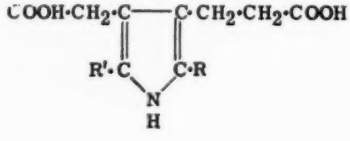
The oxidation of naturally occurring fatty acids in homogenates of several nonhepatic tissues was demonstrated by Weinhouse *et al.* (99). Specifically, palmitic acid-1-C^{13} produced $C^{13}O_2$ when incubated with homogenates of pigeon breast muscle, pigeon heart, rat heart, and rat kidney. The results suggest that higher fatty acids produce more CO_2, relative to acetoacetate production, than do the shorter fatty acids such as octanoate. In washed

liver homogenates, fumarate was found to accelerate oxidation of palmitate to carbon dioxide, thus confirming previous evidence implicating the tricarboxylic acid cycle in the oxidation of the natural fatty acids.

Porphyrin Metabolism

The discoveries by Bloch & Rittenberg (100) and Shemin & Rittenberg (101) that acetate and glycine were utilized for the biosynthesis of protoporphyrin have stimulated numerous investigations in the field of porphyrin metabolism. Shemin *et al.* (102), seeking a porphyrin-forming system less complex than intact animals, found that duck blood can synthesize hemoglobin *in vitro*. The rate of hemoglobin synthesis was found to be approximately 0.4 per cent per day, a synthetic rate in the same order of magnitude as obtains *in vivo*. This system can synthesize not only the porphyrin moiety of hemoglobin but also the globin, for these authors demonstrated that N^{15}-labeled histidine was incorporated into the protein at a rate similar to that of porphyrin synthesis. The circulating blood cells of the duck differ from those of the human in that they are nucleated and up to 20 per cent of them are reticulated. It is probably the reticulocytes which contain the synthetic mechanism, for London *et al.* (103) found that the blood of phenylhydrazine-poisoned rabbits, which contains a large number of nonnucleated reticulocytes, is capable of synthesizing heme *in vitro*. Such synthesis does not occur on incubation of either normal human or rabbit blood. The results indicate that the amount of hemoglobin synthesized in mammalian red cells after they enter the circulation must be small. In neither of the above researches could heme formation be demonstrated under anaerobic conditions, nor with hemolyzed cells.

Radin *et al.* (104) have investigated the utilization of two doubly-labeled glycines, $C^{14}H_2N^{15}H_2 \cdot COOH$ and $CH_2N^{15}H_2 \cdot C^{14}OOH$ in the duck blood system. In confirmation of the results of Grinstein *et al.* (105), it was found that the carboxyl carbon atom of glycine does not appear in the newly synthesized heme. The heme resulting from experiments in which glycine-N^{15}-2-C^{14} was employed had a C^{14}/N^{15} ratio indicating that eight alpha-carbon atoms of glycine appear in the newly synthesized heme. This has been confirmed by Wittenberg & Shemin (106) and by Muir & Neuberger (107) by degradation of protoporphyrin obtained from a similar experiment. Radin *et al.* found that neither glycollic acid, iminodiacetic acid, pyruvic acid, serine, acetic acid, or formic acid are on the direct pathway involved in the utilization of methyl carbon of glycine for heme synthesis. They suggest as a possible intermediate in porphyrin synthesis a tetra-substituted pyrrole:

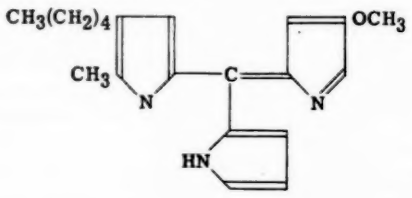


Cyclization of four of these molecules should lead to a uroporphyrin which by decarboxylation and dehydrogenation could yield protoporphyrin.

Radin *et al.* (108) have investigated the utilization of both carboxyl- and methyl-labeled acetate for heme synthesis in the duck blood system. They simultaneously administered N^{15}-labeled glycine to obtain a measure of heme synthesis. From the ratio of the incorporation of C^{14} and N^{15} in the heme, they deduced that six methyl carbon atoms of acetate were utilized for each carboxyl carbon atom and that most of the carbon atoms of heme are derived from acetate and glycine. Such quantitative deductions were possible only from experiments wherein the multiple labeling technique was employed.

The metabolic interrelationship of glycine and serine raised the possibility that glycine might be converted to serine prior to utilization for protoporphyrin synthesis. Shemin *et al.* (109) demonstrate that such is not the case. Rather the efficient utilization of serine for heme synthesis is the result of the rapid conversion of serine to glycine (110). Acetyl glycine is not used for heme synthesis in the duck blood system (109). Hale *et al.* (111) find that coproporphyrin III, which is formed by *C. diphtheriae* when cultured under conditions suitable for toxin production, is formed from N^{15}-labeled glycine. They discuss the possible route for the synthesis.

Bacillus prodigiosus produces a pigment, prodigiosin, to which the following structure has been assigned (112):



Hubbard & Rimington (113) have studied the biosynthesis of this interesting pigment from each carbon atom of acetate and from each carbon and the nitrogen of glycine. They find that both carbon atoms of acetate and both the nitrogen and the alpha-carbon atom of glycine are specifically utilized in the biosynthesis of prodigiosin, while the carboxyl carbon atom of glycine is not used. In these respects, the utilization of glycine and acetate closely resembles that observed in heme synthesis.

The relationship of hemoglobin to bile pigment in normal and pathological conditions has been extensively studied this year. London *et al.* (114) have studied the N^{15} concentrations in hemoglobin and fecal stercobilin in a normal man fed N^{15}-labeled glycine. Analyses of their data show that the major portion of the stercobilin was derived from the hemoglobin of mature circulating erythrocytes. At least 11 per cent, however, was derived from some other source. The authors suggest that direct synthesis of bile pigment may occur via a pathway which does not involve degradation of a porphyrin ring. Another possibility is that heme or porphyrin which has not been

utilized for hemoglobin production is directly converted to bile pigments.

In support of the latter view, London (115) found that the administration of N^{15}-labeled hematin to a dog results in the excretion of labeled stercobilin. He estimates that at least 18 per cent of the labeled hematin was converted to stercobilin in the nine day experimental period.

Gray *et al.* (116) have observed the same isotope concentrations in stercobilin and hemoglobin of a normal subject fed N^{15}-labeled glycine, as did London *et al.* (114). They also note that an appreciable fraction of the excreted stercobilin must arise from a source other than the mature circulating erythrocyte. The amount of this fraction is greatly enhanced in congenital porphyria. Gray *et al.* (116), London *et al.* (117), and Grinstein *et al.* (118) agree that a large part of the fecal stercobilin in human congenital porphyria is derived from a nonerythrocyte source. The same three groups of investigators (117, 118, 119) have isolated coproporphyrin and uroporphyrin from the excreta of such subjects. In all cases, the N^{15} concentration at maximum is greater in the coproporphryin than the uroporphyrin. The question as to whether one of these compounds is the precursor of the other cannot be settled by the available data. The data show that the rate of formation and degradation of coproporphyrin and uroporphyrin is high. A discussion of some aspects of the problem of congenital porphyria has been presented by Neuberger *et al.* (120).

A study of the bile pigment metabolism in a case of untreated pernicious anemia by London & West (121) indicates that in this pathological state at least 40 per cent of the bile pigment is derived from a source other than mature circulating red cells. Grinstein *et al.* (122) have found in the dog that glycine is here also a specific precursor for heme, protoporphyrin, coproporphyrin I, and stercobilin and that stercobilin is in part derived from sources other than circulating hemoglobin. They suggest that coproporphyrin I is a by-product of the synthesis of coproporphyrin III and that the latter gives rise to protoporphyrin IX. Grinstein *et al.* (123) find in lead-poisoned rabbits that glycine is a direct precursor of coproporphyrin III and that this compound is not related to hemoglobin catabolism.

Measurement of Total Body Water in Man

Continuing clinical interest in the determination of total body water in the human subject is reflected by publications from three laboratories (124, 125, 126). The administration of D_2O results in a complete equilibration of deuterium with all the ionizable hydrogen atoms of the organism. This equilibration is quite rapid being complete in less than 2 hr. If the amount of D_2O injected and the concentration of D_2O in the serum after equilibration are known, it is possible to calculate from the isotope dilution the total ionizable hydrogen. The great bulk of this is due to water. However about 1 per cent of the ionizable hydrogen in the animal is supplied by hydroxyl, carboxyl, amino, etc., groups of the organic constituents of the cell system. Total water values obtained by this procedure will

be about 1 per cent too high. The advantage of this method of determination of total water resides in the fact that we use as a tracer a substance, D_2O, which is freely diffusable, nontoxic and is neither concentrated in any organ nor selectively excreted. Its only disadvantage is the difficulty of the deuterium analyses. For this reason, the method will probably be used primarily to calibrate other simpler procedures. Hardy & Drabkin (124) in a note report on 10 adult males. They state that the water contents of their subjects varied from 70 per cent to as low as 40 per cent. An inverse correlation between obesity and water content was observed. Schloerb *et al.* (125) studied 28 subjects. They observed a variation of from 46 to 70 per cent and found the closest correlation to be with surface area and oxygen consumption. London & Rittenberg (126) found in one patient that the body water was 72 per cent of body weight. Both Schloerb *et al.* and London & Rittenberg find the average time spent in the human body by a water molecule (actually a readily ionizable hydrogen atom) to be about 12 to 13 days.

Fixation of Carbon and Nitrogen

Recent tracer studies on the photosynthetic fixation of carbon dioxide are reviewed by Hendricks & Dean (177). Foster & Carson (127) investigated the incorporation of $C^{13}O_2$ into the carboxyl groups of fumarate by the mold *Rhizopus nigricans* under aerobic conditions. Twenty-one per cent of the fumarate carboxyl carbon was supplied from intracellular carbon dioxide. However the authors emphasize that such findings do not demonstrate a net synthesis of fumarate from carbon dioxide. If the catabolism of fumarate proceeds via rapidly reversible reactions involving the conversion of a fumarate carboxyl group to carbon dioxide, the availability of labeled carbon dioxide for fixation would result in production of carboxyl-labeled fumarate via the endergonic reverse reaction sequence. This carbon dioxide fixation study was done in conjunction with experiments wherein use of C^{14}-labeled ethanol provided evidence that an oxidation product of ethanol was the only immediate fumarate precursor; the data showed C^{13}-labeled carbon dioxide to be fixed by a reaction of the type $C_4 \rightleftarrows \text{pyruvate} + CO_2$. Preliminary reports have appeared on the incorporation of $C^{13}O_2$ into malate, succinate, lactate, α-ketoglutarate (128), and citrate (129).

Watt & Werkman (130) have employed C^{13}-labeled lactate, acetate, and carbon dioxide to examine the reversibility of the anaerobic dismutation reaction:

$$2CH_3COCOOH \rightarrow CH_3CHOHCOOH + CH_3COOH + CO_2.$$

In cells and cell-free extracts of the bacterium, *Micrococcus pyogenes* var. *aureus* the reaction was found to be reversible with respect to carbon dioxide as well as lactate and thus appears to provide a new mechanism for CO_2 fixation. Acetate, as such, does not participate in the reverse reaction. As in the formate fixation reaction (98), participation of acetyl phosphate is

unlikely, for addition of adenosinetriphosphate enhances formation of C^{13}-labeled pyruvate from carbon dioxide but fails to induce formation of carbonyl-labeled pyruvate from carboxyl-labeled acetate.

Wessman & Werkman (131) present evidence in support of the view that biotin functions as a coenzyme in the fixation of carbon dioxide. Addition of egg albumin or crystalline avidin inhibited the condensation of C^{13}-labeled bicarbonate with pyruvate in both lysed and acetone-treated cell preparations from *Micrococcus lysodeikticus*. Addition of biotin restored the original oxaloacetate-forming activity.

The fixation of elementary nitrogen by illuminated *Rhodospirillum rubrum* cells was studied by Wagenknecht & Burris (132). After aeration with N^{15}-enriched N_2 for 30 min., the cells were inactivated with acid, the proteins hydrolyzed, and amino acids separated on a starch column. The compound showing greatest N^{15} enrichment was ammonia. Isotope distribution among the amino acids was similar to that previously observed with *Azotobacter vinelandii;* an alanine-glutamic acid mixture and aspartic acid contained the highest concentration of N^{15}, and lysine, histidine, and cystine were lowest in N^{15} enrichment.

The discovery that rhizobia do not participate in the symbiotic fixation of nitrogen with cow pea and soy bean nodules (133) has stimulated further studies to ascertain the basis for earlier reports showing fixation to occur in the nodules. Tove, Niss & Wilson (134) showed that surface sterilization is not always effective in removing the nitrogen-fixing (135) anaerobe *Clostridium*. The fixation of $N^{15}{}_2$ by excised nodules containing clostridia was usually small, and the presence of oxygen, the number of contaminants, and especially the supply of soluble combined nitrogen apparently controlled the rate of fixation.

Miscellaneous

Methyl groups.—Choline has received considerable attention as a source of "labile methyl groups" and is frequently represented as a member of the B complex of vitamins. Animals suffering from a methionine deficiency are restored to health and normal growth if their diets are supplemented with choline and homocysteine (136); if methyl-labeled choline is used, a high concentration of isotope appears in the methyl groups of the resulting methionine and creatine (137). Some evidence (138) has indicated, however, that choline per se does not tranfer its methyl groups, an oxidation product, betaine, being the effective methyl donor. The findings of Muntz (139) support this view. When N^{15}-choline was incubated anaerobically with rat liver homogenates and homocysteine, methionine was formed, but dimethylaminoethanol, the theoretical demethylation product of choline, did not appear. Instead, the demethylation product of N^{15}-betaine, N^{15}-dimethylglycine was formed. The biological synthesis of the "labile methyl groups" of choline and methionine has been demonstrated by du Vigneaud *et al.* (140). When D_2O was administered to normal or germ-free rats, deuterium was

found in the methyl groups of methionine and choline; the findings of this study exclude the possibility that such synthesis is performed only by the bacteria in the body. Although the "labile methyl groups" were once considered to be available only from dietary sources, it has now become clear that the body can synthesize the entire choline molecule and some of its required methyl groups provided that the diet contains an adequate supply of the vitamins B_{12} and folic acid (16, 141, 142, 143).

Carbohydrates.—The role of lactate in glycogen synthesis has been studied by Lorber *et al.* (144). Sodium lactate-2,C^{13}, lactate-2,3-C^{13}, and lactate-2-C^{13}-3-C^{14} were fed to fasted rats, and the isotope distribution of glucose from liver glycogen determined. The alpha-carbon of lactate was metabolized to form glucose containing about 40 per cent more isotope in the 2,5 positions than in the 1,6 positions, whereas the beta-carbon gave rise to an isotope concentration 10 to 20 per cent higher in the 1,6 positions. Carbons 3 and 4, conventionally arising from the carboxyl groups of lactate, always had roughly one-fourth the isotope enhancement of the other positions. The results are interpreted as providing further evidence that the phosphorylation of pyruvate and reversal of glycolysis proceed slowly relative to the reversible carboxylation of pyruvate and equilibration of the resulting dicarboxylic acid with fumarate.

The partial randomization of isotope between alpha and beta-carbon atoms which has been observed with lactate (144) and pyruvate (145) was shown to be a quantitative process when alpha- or beta-labeled propionate (146) is employed for glycogen synthesis. A net reaction involving addition of CO_2 to the beta-carbon of propionate to form succinate was advanced to explain both the glycogenic properties of propionate and the distribution of isotope in the glucose units.

The ingenious suggestion of Ogston (147) that symmetrical molecules such as citric acid, might undergo an asymmetric reaction in an enzymatic system, has profoundly affected the interpretation of isotopic experiments. Several experiments (148, 149) have been carried out to verify this hypothesis. Martius & Schorre (150) prepared dideuterio citric acid (I) by treating the lactone of citroylformic acid (II) with D_2O and D_2O_2. Three samples of deuteriocitric acid were prepared from the *dl*, *d*, and *l* isomers of the lactone. On enzymatic degradation of the deuteriocitric acid, it was found that the citric acid prepared from the *d* isomer of the lactone of citroylformic acid

I II

produced an α-ketoglutaric acid containing the same amount of deuterium as the starting citric acid. The ketoglutaric acid derived from citric acid prepared from the *l*-isomer contained no deuterium, while the α-ketoglutaric

acid derived from the *dl*-lactone contained half the amount of deuterium as had been present in the deuteriocitric acid. These results clearly show that the oxidation of citric acid by the enzyme system proceeds asymmetrically as predicted by Ogston.

Urea.—While the broad aspects of the biochemical mechanism involved in the synthesis of urea are understood (151) the details of this process remain obscure. Ratner & Pappas (152) have demonstrated, in a series of elegant experiments, that an enzyme system can be prepared in which citrulline is aminated by aspartic acid to yield arginine. These authors suggest that this route is the principal one employed in urea synthesis. Nitrogen from various sources is used to form aspartic acid which then aminates citrulline to yield arginine. Hirs & Rittenberg (153) using various N^{15}-labeled substrates have studied the formation of urea in surviving rat liver slices. In confirmation of Krebs & Henseleit (151), they find that ornithine functions almost exclusively as a catalyst in the synthesis of urea, that citrulline is an intermediate in the reaction in the manner formulated by Krebs & Henseleit and that the amide groups of glutamine is not an important source of urea nitrogen. Their experiments show that, while the nitrogen of aspartic acid can be directly used for urea synthesis, ammonia is by far the most efficient source of urea nitrogen. The cause of the apparent discrepancy between the results of Ratner & Pappas and those of Hirs & Rittenberg is not immediately obvious. It is possible that the findings of the latter authors reflect the existence of diffusion barriers in the cell which prevent ready access of aspartic acid to the intracellular urea-forming system. Ammonia, for which no diffusion barrier exists, would then enter the cell and be used for the formation of aspartic acid; the latter would then be used in the Ratner-Pappas mechanism. However, Hirs & Rittenberg offer evidence that aspartic acid can enter the cell [cf. also (17)]. Their data is qualitative in nature, rendering it difficult to determine whether the diffusion of aspartic acid is the rate determining step. On the other hand, Hirs & Rittenberg raise the important question whether the complete loss of enzymatic organization in the enzyme extracts of Ratner & Pappas may have resulted in the loss of regulatory mechanisms. If citrulline could be aminated to arginine by more than one substance, i.e., ammonia, as well as aspartic acid, under the action of different enzyme systems, it is possible that the fractionation process could have separated the system of Ratner & Pappas from other existing systems. If the rate determining factor in urea formation is the concentration of citrulline (154), then the single enzyme system could produce as much urea as the complete system in the intact cell. Such data could then be interpreted to indicate that this single system represents the main physiological pathway of arginine synthesis and urea formation. The resolution of the difficulty requires further work, especially determinations of the rate of diffusion of various amino acids into the liver cell.

Berenbom *et al.* (155) offer an experimental test of the modification of the isotope dilution method (156) proposed by Bloch & Anker (157). This method

permits the simultaneous determination of the amount of a compound present in a mixture and its isotope concentration. The method is applied to the determination of the amount and N^{15} concentration of urea in urine.

Plants.—Labeled nitrogen compounds have been employed in several studies on the sources of nitrogen in plant tissue. When clover, tobacco, and tomato plants were grown under aseptic conditions, it was found that the plants initially utilize their reserves of seed nitrogen, then employ nitrogen from ammonium salts, and finally use some nitrogen from certain amino acids (158). Field experiments wherein 20 to 40 lb. $(N^{15}H_4)_2SO_4$ per acre were used as fertilizer for growing oats showed that 4.7 to 17.9 per cent of the total plant nitrogen came from the fertilizer (159).

Mendel, Visser & Winzler (160) have compared $N^{15}H_4^+$ and $N^{15}O_3^-$ as nitrogen precursors for nitrogen-deficient tomato plants. With both precursors and in all parts of the plant, the N^{15} concentration was higher in the ammonia and amide nitrogen than in the amino acids; however the N^{15} concentrations of these compounds was located mainly in the leaves when $N^{15}O_3^-$ was used, whereas the N^{15} concentrations were highest in the roots when ammonia was the nitrogen source. It is noteworthy that all of the current tracer studies on nitrogen metabolism in plants emphasize the importance of ammonia as a primary source of nitrogen for metabolic reactions in plants (132, 158, 159, 160).

Reviews.—A number of recent reviews (161 to 176) present material relevant to the varied applications of stable isotopes in biochemical research.

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RADIOISOTOPES IN SOILS RESEARCH AND PLANT NUTRITION[1]

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Higher plants are dominantly autotrophic, drawing upon their surroundings for radiant energy. They require only ions of inorganic compounds and the simple molecules CO_2 and H_2O, although some can utilize N_2 symbiotically. The inorganic ions are generally taken in through roots from soil. Plant nutrition, as it is usually considered, deals with ionic absorption and utilization by plants. Soil science, particularly in its fertility aspects, and agronomy are concerned with the supply of the ions to the roots of the plants. Isotopic tracers can be used to advantage in following the behavior of a particular element in soil, its transfer to plants, and its transport and ultimate functioning in plants. The discussion presented here will be restricted in this sense. Biochemical work on photosynthesis, nitrogen fixation and metabolism, and transformation of carbon compounds, as involved, for instance, in the synthesis of rubber, accordingly will not be treated.

Transport of mineral nutrients from roots to shoots and subsequent redistribution within plants can readily be followed by use of radioisotopes. Striking qualitative information can be obtained from radioautographs either made from entire plant parts or from sections (51) and particular tissues can be removed for quantitative radioactive assay. Very few of these autographs have appeared in publications but collections of them are being made by several groups. An example from earlier work is given by Thomas' study(64) of sulfur and arsenic distribution in tomato, sugar-beet, and other crop plants. He found that S^{35} supplied as the sulfate to sugar-beet roots accumulated in the cambium and phloem of the beet rather than in the xylem and was present to a greater extent in young rather than old leaves. The tomato fruit took up SO_2 from the air with later distribution of the sulfur in the vascular tissue of the fruit. Translocation of sulfur taken in through the leaves was slower than that supplied by roots.

Quantitative measurements, particularly those of Hoagland and his associates (22), served quite early to settle one of the long-standing arguments of plant physiology about the extent of transport in the water-conducting and phloem elements of plants. Phosphates were found in part to move upward in the former and then undergo redistribution downward in the latter, at a rate greater than 21 cm. per hr. in the cotton plant (Biddulph, 1944). Recently Moore (40) followed the movement of phosphate from part of the roots of maize plants that were immersed in nutrient solution containing $P^{32}O_4^{---}$ into the shoot and the remaining roots that were placed in non-

[1] This review is essentially a survey of papers published in 1950.

radioactive nutrient solution. Movement to all parts of the shoots was observed after two hours, but only after six hours in the remaining roots. Downward movement to roots was greatest when they were placed in phosphate deficient medium. Some radiophosphate was lost from untreated roots into the nutrient medium. After 72 hours the activity of the treated roots was still 20 times that of the remainder. In an experiment for production of calcium phytate containing P^{32}, Withner (70) found that phosphate appeared in the foliage of maize plants near tasseling time, about six days after application to roots, and reached a maximum value after 12 days. The husks of developing ears reached a peak in activity before the enclosed ear or tassel. Later the cob lost most of its phosphate to the maturing ear.

Absorption of phosphate containing P^{32} was traced for two inbred lines of maize and their hybrids (47) in which morphological development and tissue differentiation was also followed. Greatest absorption was shown by the hybrid having the larger root system. Phosphate was at a maximum in immature internodes and decreased as the internode elongated. The advantage of the hybrid in phosphate absorption reflects earlier development, earlier maturity, and differences in vascular organization.

Malfunctioning or inadequacy of elements such as Cu, Mn, and Fe in plant growth is strikingly shown by loss in green color. Many theories have been advanced to account for this chlorosis, but none seems entirely adequate. Among these is the possible precipitation of iron at root surfaces, and the interaction of iron with phosphate and manganese. Sideris (54) found that iron was deposited in great amounts in the outer tissue of pineapple roots. High concentrations of Mn increased the deposition and decreased transport into the leaves. The final amount of iron in leaves was decreased by about 50 per cent when the Mn concentration exceeded that of iron by five fold. Biddulph (2), as a result of extensive work on iron nutrition of beans and other plants, concluded that precipitation of iron as ferric phosphate accompanying continuous movement of phosphate in plants is an important factor causing chlorosis.

The nutrition of the peanut has been followed with P^{32}, Co^{60}, and Ca^{45} (4, 19). This plant produces flowers aboveground, and the flowers after being fertilized form pegs which push into the ground and develop into fruit. Under field conditions it is observed that the fruit sometimes develops poorly even though the plant grows well. By isolating the nutrient medium of the fruiting zone from that of the roots and by using the radioisotopes indicated, uptake of calcium by the fruit was shown to be very important. Phosphorus and cobalt, on the other hand, were taken up almost solely by the roots. The calcium absorption from the plant into the developing fruit is apparently blocked and further fruit development depends upon the external supply of calcium in the fruiting zone.

Molybdenum requirements of plants which are of the order of a few parts per billion of their green weight can readily be followed with Mo^{93} and Mo^{99} (61). Roots were found to concentrate molybdenum from solutions contain-

ing less than 10^{-9} gm. per l. and the absorbed molybdate was readily translocated to the shoot. Molybdenum appears to accumulate in areas having the greatest number of stomatal openings rather than in regions of greatest metabolic activity such as growing tips. Molybdenum supplied to chlorotic Mo-deficient plants first accumulates in the chlorotic areas. Distribution of manganese in plants has also been followed (39) in its dependence on supply.

Supply of sulfur to plants in large sections of the United States depends upon absorption from products of combustion. Ten days after absorption of SO_2 by leaves of alfalfa plants more than 95 per cent of the SO_2 had been transformed into organic compounds of sulfur (1). In other experiments (63) in which sulfate was supplied through stems only 30 per cent of that taken up remained as sulfate after five days. Alfalfa plants from which tops had been cut still absorbed sulfate from a nutrient medium, but none of this sulfate was reduced to organic forms (63). Leaves reduce sulfate both in darkness and in light.

Sulfur is also widely used in fungicides, which in the case of citrus sometimes causes fruit damage. Turrell (65) found that S^{35} dusted on lemon fruit penetrates the peel to a depth of about 240 microns when incubated at 60°C. This depth corresponds to the depth of injury often observed under field conditions suggesting that sulfur dissolves in the wax coating and moves along wax channels in the fruit. Damage from SO_2 in smelter fumes also is restricted to the immediate effect on foliage (63).

Sodium is not generally considered to be an element required for plant growth but it is known to improve yields of some crops, notably sugar beets. Experiments with Na^{22} (31) indicated ready absorption by beets, radishes, oats, and other plants. Amount of absorption depended upon the potassium salt concentration in the nutrient medium, being decreased about ten-fold upon change of the K level from 4 to 195 p.p.m. Most of the sodium remained in the plant sap, as expressed with an hydraulic press, the amount varying between 58 and 92 per cent of the total. Radioautographs also indicated that the sodium remained in the vascular tissue rather than going into the more rapidly growing parts.

Transport of mineral nutrients through root surfaces that are metabolically dependent is considered to be chiefly, if not exclusively, an aerobic process. Uptake of K^{42} and P^{32} by tomato plants was found to be linearly dependent upon the logarithm of the oxygen pressure in the range of 0.5 per cent to 21 per cent oxygen (24). The rate of transport of phosphorus from the root to the shoot of tobacco, however, was independent of oxygen pressure in this range, although the uptake from the nutrient medium depended upon oxygen pressure. This possibly indicates that water uptake by tobacco roots is not dependent upon oxygen pressure in this range.

In use of radioisotopes in plant nutrition attention must be devoted to possible injury affecting the course of the nutrition and the subsequent development of the plant. Due to preferential absorption in some tissues, such as terminal meristems or at root surfaces, radioisotopes present in small

amounts in soils and nutrient media can be greatly concentrated by plants. Genetical effects of high energy radiation on living material have long been studied and have been shown to arise both from gene mutation and chromosome breakage. Some of the more recent findings have been summarized in symposia (23). In plant nutrition, however, one is chiefly concerned with the response of the sporophyte that might be considerably involved with extra nuclear effects of radiation.

Effects of P^{32} on increase in dry weight of young barley plants growing on nutrient media at initial concentrations of 0.5 to 50 μc. per l. were measured by Russell & Martin (50). They found a 5 to 10 per cent reduction in dry weight relative to controls for roots at 0.5 μc. and about 40 per cent reduction at 50 μc. when the initial phosphate concentration was less than 10^{-2} milliequivalent $H_2PO_4^-$ per l. Retardation of root growth was about 10 per cent less than these values at initial phosphate concentrations of 1 m.eq. $H_2PO_4^-$ per l. and this was also the case for shoot growth. Measurement of radioactivity in root tips indicated that P^{32} could be concentrated as much as thousandfold over that of the dilute medium. This work was later repeated in its essential points (49) and extended to winter wheat growing in soil to which phosphate had been added at the rate of about 40 lb. per A with initial P^{32} activities of 30, 300, and 3,000 μc. per gm. P_2O_5. No significant effects were noted on dry weights of harvested plants at any of the rates used. Amounts of phosphate absorbed from the fertilizer, however, were reduced by about half at the two higher levels in comparison with the lower level. In field work wheat fertilized with phosphate at the rate of 48 lb. P_2O_5 per A initially containing as much as 0.65 mc. per gm. of P^{32} Dion and co-workers (11) obtained no significant change in growth. This was also the case in later field experiments in which $NH_4H_2PO_4$ was applied at rates of 12, 24, and 48 lb. P_2O_5 per A with initial activities of .90 mc. per gm. P_2O_5. Lethal effects (57) on germinating wheat, barley, and sunflower seeds were found with absorption of about 1.4 μc. of P^{32} or Sr^{90} per seed.

Blume, Hagen & Mackie (5) have measured growth responses of young barley plants grown on nutrient solutions containing 0 to 200 μc. P^{32} per l. with total phosphate concentrations from 5×10^{-6} to 1×10^{-3} *M*. Injury as shown by histological examination and by growth response was not observed below P^{32} levels maintained at 5.6 mc. per gm. P_2O_5. In experiments with barley growing on nutrient solutions maintained at levels of 0, 2, 4, 8, 16, 32, 64, or 128 μc. P^{32} per l., decrease in dry weight of tops relative to untreated controls was first noted at 16 μc. for a nutrient concentration of 2×10^{-5} molar phosphate and none was observed even at the 128 μc. level in 1×10^{-3} molar phosphate. At the higher P^{32} concentrations cell division at the root tips and terminal meristems of the shoots was reduced and the cells enlarged above normal. In later work (unpublished), increased cell size at the apex of the terminal bud was present even at the 2 μc. P^{32} level for low phosphate concentrations.

These experiments indicate that P^{32} can safely be used in plant work at

concentrations below 0.2 mc. per gm. P_2O_5 initial activity. Most work is conducted below this level. Very few observations have been made on injury arising from use of other radioisotopes with plants. Plutonium absorbed on root surfaces was observed to affect the development of dwarf pea plants(27).

Supply of mineral nutrients from soils to plants is tempered by chemical interactions of the ions concerned with surfaces of soil particles either to form surface compounds or new phases. This is true for important cations such as K^+ and Ca^{++}, as well as anions such as phosphates and minor nutrient elements like zinc and iron. Equilibration of cations between solutions and exchange materials such as soils, resins, and clay minerals can readily be followed with radiocations. Krishnamoorthy & Overstreet (35) used K^{42}, Ca^{45}, Rb^{86}, Cs^{137}, and La^{140} in this way to test the validity of several expressions for the equilibrium of reactions such as:

$$NH_4 - \text{clay} + ACl \rightleftarrows A - \text{clay} + NH_4Cl.$$

Approach to within 1 per cent of equilibrium was attained in all cases within a few minutes. The exchange equilibrium can best be expressed by an equation based on statistical distribution between available sites on the clay and the solution. Rapid attainment of equilibrium was also shown for solutions containing Ca^{45} with the calcium ion exchange compounds of the clay minerals kaolinite, halloysite, illite, beidellite, and montmorillonite (62) that are commonly present in soils. This rapid exchange is essentially the reason why cations will not move appreciably in any save the sandiest soils, which is important in localizing radioions applied in the field.

Phosphates are also strongly held against movement in soils while still being available in varying degrees to plants. The nature of the phenomena involved is one of the continuing questions of soil science. McAuliffe and coworkers (38), in a first approach to the problem making use of P^{32}, found that a part of the soil phosphate rapidly equilibrates by exchange with an ambient solution. The amount of this rapidly equilibrating surface phosphate parallels levels of fertility for phosphate. A slower, less reversible exchange of phosphate was also noted. Both processes seem to involve diffusion of anions over surfaces of soil particles, the simple exchange reactions being very rapid. Coleman (9), from studies of reaction rates between phosphate on surfaces and in solution, from the equilibria attained, and several other criteria, found that about 2.5 mg. phosphorus per gm. of clay on the surface saturated a similar type of reaction for several clays. This corresponds to about 4×10^{19} molecules on surfaces probably exceeding $10^{21} A^2$ and would probably be compatible with complete covering of the hydroxylic surface. Seatz (53) found, in agreement with previous observations, that arsenate in neutral solutions is particularly effective in displacing phosphate from clays but that even after repeated extractions only about half of previously equilibrated $P^{32}O_4^{---}$ can be removed. Surface reactions of mineral apatites, which are the essential compounds of bone, are also important in soils since they might either naturally be present, be added as fertilizers, or later be formed in soil

from added phosphates. While much work is in progress, that reported in the literature is restricted to work on skeletal materials (15) that demonstrated a rapid surface exchange of phosphate (43). In some preparations one out of five calcium ions in the phosphate salt of bone could be exchanged with Ca^{45}.

The concept is held that in ion uptake by roots the first step is an exchange reaction between the root surface and the ambient system. Jenny & Overstreet (29, 30) advanced the theory that ions undergo such exchange from the surface of soil particles. In this way plants can draw ions from systems of large reserves even though the solution phase required for water supply has a low salt content. Williams & Coleman (69) found that the surface cation exchange capacity was from 0.26 to 0.56 m.eq. per 100 gm. of roots for several plants. They demonstrated that 97 per cent of Cs^{137} adsorbed on barley roots exchanged in 10 sec. with 0.01N $CaCl_2$ solution and 92 per cent with 0.01N CsCl solution. The exchange capacity, moreover, was closely the same for living and recently killed roots, which fact, together with the rapidity of the exchange, is indicative of a surface phenomenon. Root tips and root hair zones of soybean and root tips of corn were shown to have the highest capacity for surface uptake of Cs^{137}. In this case the radioactivity of the Cs permitted analytical sensitivity adequate for the experiment.

Absorption by plants of various radioions resulting from fission also bears on this theory of ion uptake. Vlamis & Pearson (67) found that Zr^{95} and Nb^{95}, which are not required for growth, were taken up by carrots from soils in which they were strongly held. More than 95 per cent of the activity taken up, however, remained in the root, as also had been found (27) for plutonium, yttrium, cerium, and tellurium. Zirconium and niobium radioions have also been shown to readily redistribute between solid exchange materials in contact (67). Strontium, in keeping with its similarity to calcium, is largely transported to leaves and meristematic tissue.

Sensitiveness with which radioisotopes can be determined make them valuable for following uptake by plants of minor nutrient ions such as Zn, Mn, Fe, and Cu which are normally present in soils in concentrations of a few p.p.m. Increments of change can also be followed with high accuracy over short periods which permits new types of experiments. Epstein (14) utilized these possibilities to follow the uptake by tomato plants of Zn^{++}, Mn^{++}, and Fe^{+++} present in small amounts on montmorillonite at pH 5.5 with Ca^{++} and H^{+} as principal exchange cations. The uptake increased markedly with increasing degree of saturation up to about 0.2 per cent saturation but changed relatively little at higher values. At a constant low degree of saturation, uptake of ferric and zinc ions depended linearly upon the amount of the Ca, H, and montmorillonite used. Uptake of Mn^{++} was diminished by increased degree of saturation of the montmorillonite with H^{+} while that of Zn^{++} was enhanced.

Transfer across a cellular membrane in the root is considered to be a second step in the uptake of an ion. The membrane is permeable to ions such as K^{+} (25) but the transfer is largely dependent upon metabolism of the

tissue concerned. A rather great divergence of ideas exists, however, about the nature of the dependence. Lundegardh (33) holds that anion "respiration" is metabolically determined and is accompanied by cation transport for maintenance of charge. Hoagland (22) and others, on the basis of work carried out in part with radioisotopes, consider cation transport equally to be dependent upon metabolism. Little work has been done with higher plants to establish the nature of the transport systems, although Lundegardh has shown that they are susceptible to azide and other poisons. An Fe^{+++}/Fe^{++} system such as cytochrom-cytochrom oxidase is presumably involved. Observations have been made on bacteria (48) indicating that accumulation of potassium as followed with K^{42} depends upon binding to hexose phosphates produced during carbohydrate metabolism. Jacobson *et al.* (25), continuing earlier work with radioisotopes (22), have followed the release and uptake of K^+ by barley roots by usual analytical methods, chiefly as a function of the H^+ concentration of the medium. They conclude a reaction of the type

$$HR + K^+ \rightleftarrows KR + H^+,$$

where HR is a metabolic product, is involved.

Broyer (7) followed uptake of Br^{82} by excised barley roots and found a marked decrease at 0.5°C. as compared with 20°C., as would be required for metabolic dependence. At low temperatures, with roots previously immersed in KBr solution, uptake was possibly restricted to surface exchange.

Field and Greenhouse Experiments with P^{32}

The more practical aspects of nutrient absorption from soils and fertilizers have been under consideration for many years. Such investigations have provided a basis for much of our knowledge pertaining to soil fertility and fertilizer use and their relation to crop production. Prior to the advent of isotopic techniques the only criteria of fertilizer behavior were growth responses and accompanying changes in chemical composition of plants. The basic principles for the use of isotopes in studies of nutrient absorption from soils and fertilizers have been discussed by Spinks & Barber (55) and Hendricks & Dean (20). Subsequently, similar techniques have been suggested to study root extension (32). Such techniques are of particular interest since they are equally applicable to plants grown under the controlled conditions of the greenhouse and to plants grown in the field.

During the last few years a great number of field experiments have been conducted in the United States and Canada using radiophosphorus. A discussion of some of these experiments was prepared by Parker (46). Several conditions have contributed to restricting these investigations to the nutrient element phosphorus: namely, the desirable characteristics of the isotope P^{32}, the restrictions on using isotopes with a long half life in the field, and the universal importance of phosphorus as a fertilizer constituent.

The methods used for field or greenhouse experiments to study the utilization of phosphorus from fertilizers are essentially the same and, briefly, are

as follows (10, 41). A fertilizer is synthesized to contain P^{32}. This material is placed in the soil and the crop to be investigated is grown. Plant samples are collected at the desired stages of growth. The relative specific activity of these plant samples is determined and under standard conditions compared to that of the original fertilizer. In experiments with phosphorus, if the specific activity of the plant samples equals that of the fertilizer, the conclusion would be that all of the phosphorus entering the plant came from the fertilizer. On the other hand, if the specific activity of the plants is only half that of the original fertilizer then it is assumed that only half of the phosphorus entering the plant was derived from the original fertilizer and the other half was derived from soil sources. Thus the basis for these experiments is the assumption that the technique provides a method for measuring the relative proportion of soil and fertilizer phosphorus entering the plant.

One of the prerequisites for the experiments described above is a relatively large supply of fertilizer materials containing P^{32}. Further, the properties of these materials should be identical with the commercially available product they are to represent. To meet this demand facilities and methods have been developed by the Bureau of Plant Industry, Soils and Agricultural Engineering (21). Also, special machinery for applying the fertilizer in the field has been developed (8).

TABLE I

THE PERCENTAGE OF PHOSPHORUS IN CROPS DERIVED FROM THE FERTILIZER AT VARIOUS STAGES OF GROWTH*

Crop	Days after planting			
	30	60	80	100
Potatoes	50	65	62	—
Soybeans	45	35	27	22
Corn	77	30	27	24

* Adapted from Krantz *et al.* (34).

Experiments in the use of fertilizers have shown differences in the requirements of various crops grown on a given soil. In recent experiments fertilizers containing P^{32} have been applied to many crops and have revealed differences in the relative utilization of soil and fertilizer phosphorus. An experiment conducted with potatoes, soybeans, and corn grown simultaneously in the same field in North Carolina will be used as an illustration (34). Table I gives the relative amounts of fertilizer phosphorus contained in these crops at various stages of growth. In the young potato plants 50 per cent of the phosphorus was derived from the fertilizer and this increased to about 60 per cent as the plants matured. With corn the fraction of phosphorus derived from the fertilizer declined sharply as the plant matured.

This difference between crops is attributed to differences in root systems and their development. Fertilizers are normally applied in the proximity of the seed; thus in the early seedling stages important concentrations of nutrients from the fertilizer are accessible to root system. However, as the root system develops, increasing amounts of soil nutrients become accessible and are absorbed by the plant. In the case of potatoes roots are restricted to a relatively small volume of soil because of plant characteristics and the hilling operations. Thus the fertilizer contributes an important part of the phosphorus absorbed by this plant throughout the growth cycle. The general pattern of soil and fertilizer phosphorus utilization has been determined for a number of crops growing under a variety of environmental conditions including wheat (55, 56), barley (44), oats (59), sugar beets (44, 45), alfalfa (45), corn (34, 42), cotton (42), tobacco (71), potatoes (28), and soybeans (68).

TABLE II

AMOUNT OF FERTILIZER AND SOIL PHOSPHORUS ABSORBED BY CROPS*

Crop	P_2O_5 in crop from fertilizer	P_2O_5 in crop from soil
	lbs./A	lbs./A
Potatoes	14.5	9.5
Soybeans	6.4	27.4
Corn	9.0	31.0

* Adapted from Krantz *et al.* (34).

The experiment with potatoes, soybeans, and corn described above supplied sufficient information to calculate the total quantities of soil and fertilizer phosphorus removed by the crops (see Table II). It is evident that potatoes utilized over twice as much fertilizer phosphorus as soybeans, but soybeans utilized nearly three times as much soil phosphorus as did the potatoes. Since in this experiment the application of fertilizer was at the rate of 100 lbs. per A of P_2O_5 it is readily apparent that the efficiency of utilization of the fertilizer was of a low order of magnitude. In fact, one of the important points brought out by all of the field experiments with P^{32} is the low efficiency of utilization of fertilizer phosphorus by crops.

Phosphorus is applied to soils in any of a number of materials ranging from the manures to the highly concentrated commercial fertilizers. The availability to plants of the phosphorus in these is known to vary. It is of considerable economic importance to both fertilizer producer and farmer to have an accurate evaluation of the relative availability to crops of the phosphorus in the various fertilizer materials. The experiments with P^{32} have offered a new approach to this problem.

Rock phosphate is a form of fluorapatite; it is highly insoluble but when

finely ground is not uncommonly used as a soil amendment. Fried & MacKenzie (16) compared the utilization of phosphorus from this material under greenhouse conditions with that from superphosphate on soils of varying reaction (pH). The utilization of phosphorus from rock phosphate declined with increasing soil pH through the range pH 4.9 to 5.8 but remained constant for superphosphate. The comparison of the two materials was made between 700 pounds of phosphoric acid in rock phosphate and 150 in superphosphate. At these rates rock phosphate was superior to superphosphate on the most acid soil (pH 4.9), but on the least acid soil (pH 5.8) the situation was reversed.

Superphosphate is produced by treating rock phosphate with sulfuric acid. Its main constituents are monocalcium phosphate and calcium sulfate. Superphosphate is the most commonly used phosphate fertilizer and for that reason has been used as a standard base for comparison in all of the experiments dealing with the utilization of phosphate from the various fertilizer materials. With but a few exceptions this material has been found to supply as much, if not more, phosphorus to plants as indicated by the tests utilizing P^{32}. In addition, it has been observed that the utilization of phosphorus from this material is less subject to influence by the properties of the soil in which it is placed.

Mono ammonium phosphate is a highly concentrated fertilizer material supplying both nitrogen and phosphorus. It is of particular interest in those areas where transportation costs from producer to farmer are high. Extensive comparisons of this material have been made in Western Canada with wheat as a crop (12, 13). Under their semiarid conditions and on soils containing high levels of calcium, mono ammonium phosphate was shown to be the most effective of the materials studied. Evidence was also supplied to indicate that on these soils forms of phosphatic fertilizers containing no calcium would be the most effective since they are not as readily converted to the insoluble basic calcium phosphates. On the other hand, experiments in Colorado (45) with wheat, barley, potatoes, and sugar beets have shown mono ammonium phosphate to be equal to but not superior to superphosphate.

Experimental materials including dicalcium phosphate, calcium meta phosphate, and fused tricalcium phosphate have also been compared in field experiments using P^{32}. These materials are of interest to the future development of the fertilizer industry. They have been tested on the acid soils in North Carolina (18), slightly acid soils in Iowa (59) and alkaline soils in Colorado (44, 45). In respect to soil acidity the behavior of dicalcium and fused tricalcium phosphate are similar. On alkaline soils the utilization of phosphorus by plants from these materials was decidedly less than for superphosphate. However, on acid soils the difference between these materials and superphosphate was not as great, the largest differences occurring at the early stages of growth. Experiments with wheat on high calcium soils (12, 13) have shown dicalcium phosphate to be definitely inferior to either superphosphate or mono ammonium phosphate. The utilization of phosphorus

from calcium meta phosphate by crops has compared favorably with superphosphate, the possible exception being with calcareous soils where the early season uptake of phosphorus from calcium meta phosphate tends to be less.

Liquid phosphoric acid is being used in increasing quantities as a fertilizer on the calcareous soils of the Western States. It is either diluted and applied in the irrigation water or the 60 per cent acid is applied directly to the soil. In experiments at Colorado (45) liquid phosphoric acid furnished more phosphorus to alfalfa than superphosphate and with sugar beets the two materials were about equal. Studies on the distribution of phosphate in the soil showed a deeper penetration of phosphates applied as phosphoric acid in the irrigation water than for dry fertilizers applied in the proximity of the seed. In addition to these studies Ulrich, Jacobson & Overstreet (66) have also given consideration to the use of phosphoric acid in soils.

Manures including animal dung and crop residues (green manures) are used in large quantities on many farms. Although the phosphorus content of these materials is low, the large quantities generally added results in substantial applications of phosphorus to the soil. Little was known concerning the value of such phosphate addition in terms of its utilization by subsequent crops. The phosphorus in sheep manure was labeled with P^{32} and subsequently added to a soil used in a greenhouse experiment (36, 37). When phosphorus as sheep manure and as superphosphate were added to soil at the same rate, the phosphorus from superphosphate was somewhat more available early in the growth cycle. However, later in the season there was little difference between the two sources. Fuller & Dean (17) conducted a similar experiment but utilizing green manures and concluded that green manures supplied about 70 per cent as much phosphorus to the succeeding crops as did superphosphate applied on an equivalent basis.

The purchase of fertilizers is one of the farmer's largest cash expenditures in crop production and their proper use on the farm may have an important bearing on the economy of crop production. In considering problems of this nature, again it has been possible to use field experiments with P^{32} to advantage.

The rate of fertilizer application has been included as a variable in many of the experiments where the utilization of the fertilizer phosphorus was determined. The ratio of fertilizer phosphorus to soil phosphorus entering the plant was found to increase with the rate of application. However, this relationship is linear only when the proportion of fertilizer phosphorus is small. The data given in Table III show amounts of soil and fertilizer phosphorus absorbed by corn grown at two rates of fertilization and on two soils having different amounts of soil phosphorus. Increasing the rate of fertilizer application increased the amount of fertilizer phosphorus absorbed, and the amount absorbed appears to be independent of the soil phosphorus. There is also a tendency for the amount of soil phosphorus entering the plant to be independent of the fertilizer application. Thus if the rate and kind of fertilizer used is controlled, it should be possible for experiments of this kind to afford

a measure of the phosphorus fertility status of soils. Experiments regarding this point are now in progress.

Fertilizer placement is practiced in order that the efficiency of fertilizer use by crops will be enhanced. When soluble phosphatic fertilizers are put into the soil they are rapidly adsorbed. This reduces the solubility of the fertilizer and restricts the movement through the root zone. Machines have been developed which distribute fertilizer in the soil in various ways. If fertilizers containing P^{32} are used in testing these machines, considerable additional information can be obtained. Experiments of this nature have

TABLE III

AMOUNTS OF PHOSPHORUS ABSORBED BY CORN FROM SOIL AND FERTILIZER AS INFLUENCED BY RATE OF APPLICATION AND AMOUNT OF SOIL PHOSPHORUS*

Soil phosphorus soluble in acid	25 lb. per A P_2O_5 applied		100 lb. per A P_2O_5 applied	
	P_2O_5 in crop from fertilizer	P_2O_5 in crop from soil	P_2O_5 in crop from fertilizer	P_2O_5 in crop from soil
lb. per A	lb. per A	lb. per A	lb. per A	lb. per A
65	3.8	19.2	10.1	19.9
160	3.2	36.9	9.0	31.1

* Adapted from Krantz *et al.* (34).

been conducted on a variety of crops (3, 42, 45, 59, 71). In general, these experiments have shown that the utilization of fertilizer phosphorus as effected by placement is most pronounced at the early stages of growth, and the closer the fertilizer is placed to the seed the greater the utilization. However, these differences largely disappear as the crop matures. Other experiments have indicated that there is an interaction between kind of phosphatic fertilizer and method of placement (44, 45).

Side-dressing or top-dressing is frequently practiced as a method of applying fertilizers to crops while they are growing. In the past this has not been considered a very satisfactory method of supplying phosphorus to crops since it is known that phosphates penetrate soils only to a limited degree. An experiment has been reported by Stanford *et al.* (60) in which the effectiveness of top-dressing superphosphate on established meadows was studied. This method of application was found to be surprisingly effective.

Over one hundred field experiments with P^{32} are being put out during the growing season of 1951. Preliminary experiments are also being started with Ca^{45} and other radioisotopes having moderately long half lives. This technique of measuring nutrient availability to plants seems to be well-established.

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